

PROCESS FOR THE PREPARATION OF AMMOXIDATION CATALYSTS

The present invention relates to a process for the preparation of mixed vanadium, antimony and tin oxides containing a crystalline phase of SnO_2 rutile type and to their use as catalysts for the ammoxidation of alkanes.

Certain mixed vanadium and antimony or vanadium, antimony and tin oxides are known compounds. Thus FR-A-2,072,334 describes a process for the preparation of a nitrile by ammoxidation of an alkane, using various mixed metal oxides including vanadium, antimony and tin oxides. These mixed oxides are obtained by mixing various oxides in aqueous suspension and then by evaporation of the water or filtration of the suspended solid.

US-A-5,214,016 describes a different process for preparing mixed vanadium, antimony and tin oxides, consisting in preparing an aqueous suspension of a mixture of the compounds of the elements which will be present in the mixed oxides and then in calcining the mixture, the novel characteristic of this process being the use, as the tin compound, of a stannous salt of a saturated acyclic monocarboxylic acid having from 1 to 18 carbon atoms.

These processes of the prior art lead to mixed oxides which can be used as catalysts for the ammoxidation of alkanes.

However, it remains desirable for the catalytic properties of such compounds to be further improved.

The present invention provides a process for the preparation of a mixed oxide comprising vanadium, antimony and tin and corresponding to the empirical formula (I):



in which:

- a represents a whole or fractional number equal to or greater than 0.1,
- b represents a whole or fractional number equal to or greater than 0.5, and

- x represents a whole or fractional number determined by the oxidation states of the other elements, said mixed oxide exhibiting X-ray diffraction lines characteristic of a crystallographic phase of the SnO_2 rutile type, which process comprises:

- dissolving vanadium, antimony and tin compounds in at least one saturated alcohol,
- contacting the alcoholic solution thus obtained with an aqueous solution comprising an ammonium salt, in order to precipitate the mixed oxide, and
- separating and calcining the mixed oxide.

Characterization of the crystallographic SnO_2 rutile phase is carried out by X-ray diffraction analysis, the lines characteristic of the phase of SnO_2 rutile type corresponding to the following lattice spacings d (in Å):

3.33-3.35
2.62-2.64
2.37-2.38
1.74-1.76
1.66-1.67
1.57-1.59
1.48-1.50
1.40-1.43

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

- a represents a whole or fractional number equal to or less than 100, and
- b represents a whole or fractional number equal to or less than 100.

Preference is still more particularly given to the mixed oxides of formula (I) for which:

- a represents a whole or fractional number from 0.5 to 50, and
- b represents a whole or fractional number from 1 to 40.

The vanadium, antimony and tin compounds 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. These compounds can be introduced together; they can also, first of all, be dissolved separately in an alcohol, the various alcoholic solutions thus obtained then being mixed with each other. Generally, but non-limitingly, an alcoholic solution is prepared by dissolving the various compounds, without intermediate preparation of solutions of each of the vanadium, antimony and tin compounds.

Mention may be made, as examples of soluble vanadium compounds, of vanadyl acetylacetonate, vanadyl 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 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 or stannous bromide.

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 alcoholic solution obtained above is then mixed with an aqueous solution comprising an ammonium salt, in particular an ammonium carboxylate (for example, acetate, citrate or tartrate), ammonium oxalate, ammonium carbonate or ammonium hydrogenphosphate, so as to precipitate the mixed oxide. Preferably the mixture thus has a pH of from 5 to 9, more preferably in the region of 7. Use of ammonium acetate

at a concentration of two moles per litre in water can provide a pH in the region of 7.

In order to maintain the pH of the solution preferably at a value in the region of 7, it may be necessary to progressively neutralize the acidity possibly formed during the precipitation of the mixed oxides (for example, a hydrohalic acid formed when an antimony halide and/or a tin halide and/or a vanadium halide is/are used) using a basic compound. It is preferable, in the process of the invention, to carry out this neutralization by controlled progressive addition of aqueous ammonia.

After precipitation of the mixed oxides of the invention, they can be separated from the saturated alcohol/water liquid by any technique commonly used for this type of operation, in particular by filtration. The isolated mixed oxides are then generally dried, for example at atmospheric pressure or at reduced pressure, at a temperature of for example, from 30°C to 200°C, without these values being of critical importance.

The mixed oxides of formula (I) are then calcined, preferably at a temperature of 400°C to 800°C. The calcination is more preferably carried out at a temperature of 500°C to 750°C.

The present invention also provides a process for the ammoxidation of alkanes in the vapour phase in the presence of a solid catalyst comprising at least one active phase, wherein said active phase comprises at least one mixed oxide of the empirical formula (I) which has been prepared by the process as defined above.

In general an alkane having from 3 to 12 carbon atoms per molecule is reacted in the vapour phase with ammonia and oxygen in the presence of the above catalyst.

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. The reactive gas (alkane, ammonia, oxygen) can thus be diluted with an inert diluent and/or with steam. In this grouping, the content of steam can vary within

wide limits, in particular from 0 to 50 vol% and, preferably, between 3 and 30 vol%. For a good implementation of the process according to the invention, the content of reactive gas will be at least 3% and preferably at least 20 vol%.

Within the reactive gas, the respective contents of alkane, ammonia and oxygen can vary within wide limits.

The alkane content in the reactive gas is preferably from 5 to 70 vol%. The ammonia content is preferably from 3 to 50 vol% and the oxygen content is preferably from 3 to 45 vol%. For a good implementation of the process according to the invention, the composition of the reactive mixture will be outside the explosive region. Regarding the ammoxidation of propane in the absence of inert diluent, the composition (propane, oxygen, ammonia) will be advantageously chosen from inside the quadrilateral ABDE which appears in the ternary diagram ABC represented in appended Figure 1.

In this ternary diagram, segment AB represents the ammonia content from 100 to 0 vol%; segment BC represents the propane content from 100 to 0 vol%; segment CA represents the oxygen content from 100 to 0 vol%. Point D, situated on segment BC, corresponds to a propane content of 45 vol% in the binary system (propane/O₂); point E, situated on segment AC, corresponds to an ammonia content of 79 vol% in the binary system (ammonia/O₂).

Segment DE delimits the ternary diagram as two parts: a triangle CDE within which is situated the explosive region (determined at 1 bar and at 25°C) and a quadrilateral ABDE within which the composition of the reactive gaseous mixture will be advantageously chosen.

Regarding the ammoxidation of propane in the presence of inert diluent gas(es) and/or of steam, it is advisable to determine the composition of the ternary mixture (propane, oxygen and ammonia) in order to situate it on the abovementioned diagram, when the diluent gas and/or the steam is in low proportion.

Regarding the ammoxidation of propane by means of air as the oxygen source, the composition (propane, air and ammonia) will be advantageously chosen inside the quadrilateral ABFG which appears within diagram ABC

represented in appended Figure 2.

In this second diagram, segment AB represents the ammonia content from 100 to 0 vol%; segment BC represents the propane content from 100 to 0 vol%; segment CA represents the air content from 100 to 0 vol%. Point F, situated on segment BC, corresponds to a propane content of 16 vol% in the binary system (propane/air); point G, situated on segment AC, corresponds to an ammonia content of 35 vol% in the binary system (ammonia/air).

Segment FG delimits the ternary diagram as two parts: a triangle CFG within which is situated the explosive region (determined at 1 bar and at 550°C) and a quadrilateral ABFG within which the composition of the reactive gaseous mixture will be advantageously chosen.

This second diagram will be used in the case where the oxygen/diluent gas mixture corresponds to an oxygen content equivalent to that of the air ($\approx$ 21 vol% oxygen) or in the case where this mixture is deficient in oxygen with respect to the air.

Starting from propane, a mixture will be obtained containing essentially propylene and acrylonitrile. Acrylonitrile is an intermediate produced industrially on a large scale. Propylene is a starting material traditionally used to produce acrylonitrile and various other intermediate products well known to those skilled in the art.

Starting from isobutane, a mixture will be obtained containing methacrylonitrile and isobutene or n-butenes.

The process according to the invention is more particularly suitable for the ammoxidation of propane.

If the alkane used is of technical quality, it will not contain significant amounts of compounds containing ethylenic unsaturation. Thus, the propane involved will generally only contain trace amounts of propylene, for example less than 10 vol%.

The process according to the invention is a vapour phase reaction. Consequently, any device suitable for carrying out ammoxidation or oxidation reactions in the vapour phase can be used. The process can be carried out continuously or noncontinuously and it can comprise the use

of a stationary bed or of a fluidized bed.

The reaction temperature is generally from 300°C to 550°C, preferably from 400°C to 500°C.

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

The gas flow rate is fixed such that the hourly volume rate is generally from 100 to 36,000 h⁻¹, preferably from 200 to 20,000 h⁻¹.

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

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

The catalyst used in the process for the ammoxidation of alkanes can comprise solely one or a number of mixed vanadium, antimony and tin oxides as defined above, constituting the active phase of the catalyst, or can additionally comprise an inorganic oxide, such as, for example, alumina, silica, silica/alumina, zirconia, cerite, magnesia, titanium oxide or niobium oxide, on which the said active phase is deposited or with which the active phase is mixed, by using various techniques known to those skilled in the art, such as impregnation or slurry deposition.

The catalytic phase, consisting of the active phase alone or of the active phase deposited on an inorganic oxide or mixed with the said inorganic oxide, can then be used in bulk form or in a particulate state; it can therefore be used in powder form or be shaped, for example as balls, pellets, extrudates or crushed particles, according to various known techniques.

For use of the process in a stationary bed, these techniques can be, for example, pelleting or coating on an inert substrate or on a ceramic or metal substrate of monolithic type.

For use of the process in a moving bed or in a fluidized bed, the catalytic phase is generally formed by

atomization, drying and calcination.

The catalytic phases can, for example, be shaped by compression, so as to obtain pellets. These pellets can then optionally be crushed into fragments. The precise values of the pressure, diameter and thickness of the pellets and particle size of the fragments can be chosen by those skilled in the art according to the pressure drop acceptable in the reactor.

A variant of the preparation of the catalytic phase can consist in carrying out, in a single stage, the synthesis of the active phase and its deposition on an organic oxide or its mixture with the said inorganic oxide.

The catalytic phases can also be deposited on an inert support or can coat it. The nature of this support is not critical so long as it is chemically inert with respect to the reactants under the chosen reaction conditions.

By way of examples of supports suitable for the preparation of catalysts which can be used in the context of the process according to the invention, there may be mentioned: silica, alumina, silica/alumina, sintered clay, carborundum, magnesia, magnesium silicate and diatomaceous earth. This support is preferably nonporous and can be especially based on a refractory oxide in particulate form, the most commonly employed support being clay-based. This support can, for example, consist of inert, complete, solid and rough clay balls with a diameter of from 0.5 to 6 mm. The precise value of the diameter of the balls can be chosen as a function of the acceptable pressure drop in the reactor. This support can also be made nonporous by enamelling.

This support can also be a ceramic substrate, preferably in the form of an inert and rigid structure of a monolithic type comprising channels or ducts. Such supports are well known and have been widely described in the literature. The substrates used which are made of ceramic substance are especially those comprising, as the main substance, cordierite, alumina, mullite, porcelain, and the carbides of boron or silicon.

This substrate can also be a metal substrate. Such substrates are well known. Suitable metal substrates are in

particular those obtained from iron, nickel and chromium alloys or those obtained from iron, chromium, aluminium and cobalt alloys, such as those known under the trade name Kanthal, or those obtained from iron, chromium, aluminium and yttrium alloys, known under the trade name Fecralloy. The metal can also be carbon steel or simple cast iron.

When a coated catalyst is resorted to, the amount of catalytic phase, which can vary within wide limits, is in practice between 1 and 50 vol% and, preferably, between 5 and 35 vol% by weight with respect to the support + catalytic phase combination.

Thus, certain catalysts, useful for an implementation of the process in a stationary bed, can be obtained by coating the crushed, intermediate or finished, catalytic phases in a way known per se. This conventional method consists in depositing a layer of intermediate or finished catalytic phase around inert but rough balls. Once the balls are covered with the desired quantity of the catalytic phase, they are dried with hot air at from 70 to 150°C for at least 30 minutes and then introduced into an oven in order to be calcined at from 300 to 600°C, preferably from 450 to 500°C, for at least 3 hours.

Certain catalysts which are useful for an implementation of the process according to the invention in a moving bed or fluidized bed can be obtained by the technique, known per se, of drying by atomization, preferably in a nonreducing atmosphere. By such an operation, followed if appropriate by calcination at a temperature of the order of 400 to 800°C, powders are obtained which are spherical in shape and have a diameter of from 5 to 700 μm . Powders consisting of at least 80% by weight of particles whose sizes are from 5 to 200 μm are preferred in the context of use in a fluidized bed.

The catalytic phase, alone or thus used in bulk form or in a particulate state, constitutes the catalyst.

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 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, CO_2 . The acrylonitrile and hydrocyanic 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.

The Examples below further illustrate the present invention.

EXAMPLES OF THE PREPARATION OF MIXED OXIDES

EXAMPLE 1 - Preparation according to the invention of the mixed oxide (A) of following empirical formula:
 $\text{VSb}_{3.3}\text{Sn}_{3.3}\text{O}_x$

A solution of 15 g of anhydrous SnCl_4 , 4.57 g of vanadyl acetylacetonate and 17.22 g of SbCl_5 in 100 ml of absolute ethanol is prepared.

The ethanolic solution is poured dropwise into 500 ml of aqueous solution containing ammonium acetate (2 mol/litre) in order to have an initial pH of the order of 7.0. During the precipitation of the mixed V, Sb and Sn oxides, the pH, which tends to decrease due to the release of hydrochloric acid, is kept constant by addition of a concentrated aqueous ammonia solution (containing 30 % by weight).

The precipitate thus formed is isolated by filtration, washed with water, dried for 12 h at 140°C and then calcined for 3 h at 700°C .

The compound of formula $\text{VSb}_{3.3}\text{Sn}_{3.3}\text{O}_x$ thus obtained is then compressed under a pressure of 4300 bars. Pellets with a diameter of 3 cm and with a thickness of approximately 0.5 cm are then obtained. These pellets are crushed into fragments with a particle size of between 0.3 and 0.8 cm, constituting the catalyst (A) in accordance with the invention.

EXAMPLE 2 - Preparation according to the invention of a mixed oxide (B1) of the following empirical formula: VSb₅Sn₅O₈

The mixed oxide (B1) is prepared by following the procedure described in Example 1 but using 3.05 g of vanadyl acetylacetonate and 17.22 g of antimony pentachloride.

EXAMPLE 3 - Preparation according to the invention of the mixed oxide (B2) of the following empirical formula: VSb₅Sn₅O₈

The mixed oxide (B2) is prepared according to the same procedure as in Example 2 but the calcination is carried out for 3 h at 800°C instead of 700°C.

EXAMPLES 4 TO 11 - Preparation according to the invention of different mixed oxides

Different mixed oxides are prepared by following the procedure described in Example 1 but by using different amounts of vanadyl acetylacetonate and of antimony pentachloride or by calcining at a different temperature or alternatively by using another saturated alcohol.

The amounts of vanadyl acetylacetonate (VaAA) and of antimony pentachloride, the calcination temperature and the saturated alcohol used are indicated in Table 1 below for each of the examples.

Example	VaAA	SbCl ₅	Calcination temp.	Alcohol used	Mixed oxide	
					Formula	Reference
Ex.4	1.52 g	17.22 g	700°C	ethanol	VSb ₁₀ Sn ₁₀ O ₈	C
Ex.5	0.76 g	17.22 g	700°C	ethanol	VSb ₂₀ Sn ₂₀ O ₈	D
Ex.6	0.76 g	34.44 g	700°C	ethanol	VSb ₄₀ Sn ₄₀ O ₈	E
Ex.7	0.76 g	8.61 g	700°C	ethanol	VSb ₁₀ Sn ₂₀ O ₈	F
Ex.8	3.05 g	12.05 g	700°C	ethanol	VSb _{1.5} Sn ₅ O ₈	G1
Ex.9	3.05 g	12.05 g	800°C	ethanol	VSb _{1.5} Sn ₅ O ₈	G2
Ex.10	3.05 g	17.22 g	700°C	2-butanol	VSb ₅ Sn ₅ O ₈	H
Ex.11	15.25 g	25.83 g	700°C	ethanol	VSb _{1.5} SnO ₈	I

Table 1

CHARACTERIZATION OF THE MIXED OXIDES PREPARED ACCORDING TO THE INVENTION

The mixed oxides A, B1, B2, C, D, E, F, G, H and I according to the invention were characterized by X-ray diffraction using a diffractometer of Philips P1800 trademark in the measurement range 10° to 70° in 2θ . The characteristic lines of the different oxides were then compared with the characteristic lines of the pure products reported in the International Tables of X-ray Crystallography.

The diffractograms clearly demonstrate that these catalysts are composed of a rutile phase, the unit cell parameters of which are very similar to those of SnO_2 rutile.

COMPARATIVE TEST 1 - Preparation according to a process of the prior art of the mixed oxide (J) of the following empirical formula: $\text{VSb}_{1.5}\text{Sn}_{0.15}\text{O}_x$

The mixed oxide of composition $\text{VSb}_{1.5}\text{Sn}_{0.15}\text{O}_x$ is prepared by carrying out the preparation by coprecipitation in aqueous medium.

Solutions of 2.7 g of anhydrous SnCl_4 , of 15.25 g of vanadyl acetylacetonate and of 25.83 g of antimony pentachloride in hydrochloric acid are prepared separately. These three solutions are poured simultaneously and dropwise into a 2 mol per litre aqueous ammonium acetate solution (pH of 7.0). During the precipitation of the oxides, the pH is kept constant by addition of a concentrated aqueous ammonia solution (containing 30 % by weight).

The precipitate thus formed is isolated by filtration, washed, dried at 140°C for 12 hours and then calcined for 3 hours at 700°C .

The compound of formula $\text{VSb}_{1.5}\text{Sn}_{0.15}\text{O}_x$ thus obtained is then compressed under a pressure of 4300 bars. Pellets with a diameter of 3 cm and with a thickness of approximately 0.5 cm are then obtained. These pellets are crushed into fragments with a particle size of between 0.3 and 0.8 cm, constituting the catalyst (J) not in accordance with the invention.

COMPARATIVE TEST 2 - Preparation according to a process of the prior art of the mixed oxide (L) of the following empirical formula: $\text{VSb}_3\text{Sn}_5\text{O}_x$

The mixed oxide of composition $\text{VSb}_3\text{Sn}_5\text{O}_x$ is prepared by carrying out the preparation by coprecipitation in aqueous medium.

Solutions of 15 g of anhydrous SnCl_4 , of 3.05 g of vanadyl acetylacetonate and of 17.22 g of antimony pentachloride in hydrochloric acid are prepared. These three solutions are poured simultaneously and dropwise into a 2 mol per litre aqueous ammonium acetate solution (pH of 7.0). During the precipitation of the oxides, the pH is kept constant by addition of a concentrated aqueous ammonia solution (containing 30 % by weight).

The precipitate thus formed is isolated by filtration, washed, dried at 140°C for 12 hours and then calcined for 3 hours at 700°C .

The compound of formula $\text{VSb}_3\text{Sn}_5\text{O}_x$ thus obtained is then compressed under a pressure of 4300 bars. Pellets with a diameter of 3 cm and with a thickness of approximately 0.5 cm are then obtained. These pellets are crushed into fragments with a particle size of between 0.3 and 0.8 cm, constituting the catalyst (L) not in accordance with the invention.

GENERAL PROCEDURE FOR THE AMMOXIDATION TESTS

The catalyst sample is brought beforehand to a temperature of 150°C on a measuring bench while purging with helium for 10 min, and it is then subjected to a gas flow whose composition will be specified for each example and which contains propane, ammonia, oxygen, helium and, if appropriate, steam.

The total pressure of the reaction mixture, of between 1 and 6 bar, will also be specified for each example.

The total gas flow rate is defined so as to have an hourly volume rate (HVR) of between 100 and 36000 h^{-1} , the precise value of which will be indicated for each example.

Volume of active phase: 25 cm^3 .

The principle of the ammoxidation test for propane is the following:

- 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 on the catalyst examined at the inlet temperature T_1 are calculated using relationships of the type:

conversion of propane (in mol %) = converted propane / introduced propane

selectivity towards acrylonitrile (in mol %) = propane converted to acrylonitrile / converted propane.

- The catalyst is then brought from 310 to 550°C by 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:

$DC(C_3H_8)$ = conversion of propane

$S(ACN)$ = selectivity towards acrylonitrile

$S(ACN+C_3H_6)$ = selectivity towards acrylonitrile and propylene

$S(Ammox)$ = selectivity towards acetonitrile, hydrocyanic acid and other ammoxidation by-products.

The remainder to 100 % of the selectivities correspond to the formation of CO and CO₂, and optionally methane, ethane and ethylene.

EXAMPLES OF THE AMMOXIDATION OF PROPANE

EXAMPLES 12 to 19 AND COMPARATIVE TESTS 3 AND 4

Ammoxidation of propane is carried out, as described above, by using, as catalysts, active phases composed of the mixed oxides of the invention A, B1, B2, C, D, E, H and G1 and the oxides, not in accordance with the invention, J and L.

The specific conditions used with the catalysts A, B1, B2, H, G1, J and L are the following:

- hourly volume rate = 1700 h⁻¹
- total pressure = 1.3 bar
- composition by volume of the reaction mixture:

C_3H_8 = 25 %
 NH_3 = 10 %
 O_2 = 20 %
He = 45 %

The specific conditions used with the catalysts C, D and E are the following:

- hourly volume rate = 1200 h^{-1}
- total pressure = 1.3 bar
- composition by volume of the reaction mixture:

C_3H_8 = 8 %
 NH_3 = 8 %
 O_2 = 20 %
He = 64 %

The temperature conditions and the results obtained are collated in Table 2 below.

Examples	Catalyst used	Reaction temperature (°C)	DC (C ₃ H ₆) (in %)	S (ACN) (in %)	S (ACN+ C ₃ H ₆) (in %)	S (Ammox) (in %)
Example 12	A	410	15	39	47	20
		430	21	45	49	16
		450	27	43	47	10
		470	27	41	45	9
Example 13	B1	410	9	58	68	20
		430	12	57	64	21
		450	15	60	65	15
		470	20	54	57	9
Example 14	B2	410	9	46	55	28
		430	21	45	49	16
		450	25	43	47	11
		470	24	41	45	9
Example 15	C	410	10	34	34	44
		430	15	48	48	25
		450	19	43	43	10
		470	30	36	36	8
Example 16	D	410	7	35	35	48
		430	11	47	47	37
		450	19	45	45	35
		470	21	43	43	16
Example 17	E	410	4	43	43	57
		430	7	58	58	36
		450	9	55	55	35
		470	12	58	58	23
Example 18	H	410	18	44	45	28
		430	27	51	57	12
		450	23	47	52	9
		470	26	49	54	7
Example 19	G1	410	22	28	33	9
		430	23	37	41	7
		450	26	44	48	4
		470	24	42	46	4
Comparative test 3	J	410	22	30	35	12
		430	25	37	40	9
		450	23	34	38	7
		470	22	32	40	5
Comparative test 4	L	410	8	41	47	32
		430	16	37	42	14
		450	22	40	43	11
		470	23	45	48	9

Table 2

EXAMPLE 20

Ammoxidation of propane is carried out, as described above, by using, as catalyst, the active phase composed of the mixed oxide of the invention B1.

The specific conditions used are the following:

- hourly volume rate = 1800 h^{-1}
- total pressure = 1.3 bar
- composition by volume of the reaction mixture:

C_3H_8 = 30 %

NH_3 = 10 %

O_2 = 20 %

H_2O = 10 %

He = 30 %

The temperature conditions and the results obtained are collated in Table 3 below.

Example	Catalyst used	Reaction temperature (°C)	DC(C_3H_8) (in %)	S (ACN) (in %)	S (ACN+ C_3H_8) (in %)	S (Ammox) (in %)
Example 20	B1	410	3	62	65	12
		430	4	64	69	8
		450	8	66	72	9
		470	11	67	73	8

Table 3



CLAIMS

1. Process for the preparation of a mixed oxide, comprising vanadium, antimony and tin and corresponding to the empirical formula (I):



in which:

- a represents a whole or fractional number equal to or greater than 0.1,

- b represents a whole or fractional number equal to or greater than 0.5, and

- x represents a whole or fractional number determined by the oxidation states of the other elements, said mixed oxide exhibiting X-ray diffraction lines characteristic of a crystallographic phase of the SnO_2 rutile type, which process comprises:

- dissolving vanadium, antimony and tin compounds in at least one saturated alcohol,

- contacting the alcoholic solution thus obtained with an aqueous solution comprising an ammonium salt, in order to precipitate the mixed oxide, and

- separating and calcining the mixed oxide.

2. Process according to claim 1 wherein a represents a whole or fractional number equal to or less than 100 and b represents a whole or fractional number equal to or less than 100.

3. Process according to claim 1 or claim 2 wherein a represents a whole or fractional number from 0.5 to 50 and b represents a whole or fractional number from 1 to 40.

4. Process according to any one of claims 1 to 3 wherein 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.



5. Process according to any one of claims 1 to 4 wherein the soluble antimony compound is chosen from antimony pentachloride, antimony trichloride, antimony tribromide, antimony trifluoride, antimony triiodide, antimony trioxide or stibine.

6. Process according to any one of claims 1 to 5 wherein the soluble tin compound is chosen from stannic chloride, stannous chloride or stannous bromide.

7. Process according to any one of claims 1 to 6 wherein the saturated alcohol is an alkanol or cycloalkanol.

8. Process according to claim 7 wherein the saturated alcohol is an alkanol having from 1 to 6 carbon atoms or cyclohexanol.

9. Process according to any one of claims 1 to 8 wherein the alcoholic solution is mixed with an aqueous solution comprising an ammonium salt so as to have a pH of from 5 to 9, and the ammonium salt is ammonium carboxylate, ammonium oxalate, ammonium carbonate or ammonium hydrogenphosphate.

10. Process according to claim 9 wherein the pH is in the region of 7.

11. Process according to claim 10 wherein the pH of the solution is kept at a value in the region of 7 by progressively neutralizing the acidity formed during the precipitation of the mixed oxides using a basic compound.

12. Process according to claim 11 wherein the basic compound is aqueous ammonia.

13. Process according to any one of claims 1 to 12 wherein after separation of the mixed oxide, the oxide is calcined at a temperature of 400°C to 800°C.

14. Process according to claim 13 wherein the oxide is calcined at a temperature of 500°C to 750°C.

15. Process for the ammoxidation of alkanes in the vapour phase in the presence of a solid catalyst comprising at least one active phase, wherein said active phase comprises at least one mixed oxide prepared by a process as defined in any of claims 1 to 14.

16. Process according to claim 15 wherein an alkane having from 3 to 12 carbon atoms per molecule is reacted in



the vapour phase with ammonia and oxygen.

17. Process according to claim 16 wherein the alkane is propane or isobutane.

18. Process according to claim 15 or 16 wherein, in the reactive gas, composed of the alkane, ammonia and oxygen, the alkane content is from 5 to 70 vol%, the ammonia content is from 3 to 50 vol% and the oxygen content is from 3 to 45 vol%.

19. Process according to any one of claims 15 to 18 wherein the reaction temperature is from 300°C to 550°C.

20. Process according to claim 19 wherein the reaction temperature is from 400°C to 500°C.

21. A mixed oxide whenever prepared by a process as defined in any one of claims 1 to 14.

**ABSTRACT****PROCESS FOR THE PREPARATION OF AMMOXIDATION CATALYSTS**

Process for the preparation of a mixed oxide, comprising vanadium, antimony and tin and corresponding to the empirical formula (I):



in which:

- a represents a whole or fractional number equal to or greater than 0.1,
- b represents a whole or fractional number equal to or greater than 0.5, and
- x represents a whole or fractional number determined by the oxidation states of the other elements, said mixed oxide exhibiting X-ray diffraction lines characteristic of a crystallographic phase of the SnO_2 rutile type, which process comprises:
 - dissolving vanadium, antimony and tin compounds in at least one saturated alcohol,
 - contacting the alcoholic solution thus obtained with an aqueous solution comprising an ammonium salt, in order to precipitate the mixed oxide, and
 - separating and calcining the mixed oxide.

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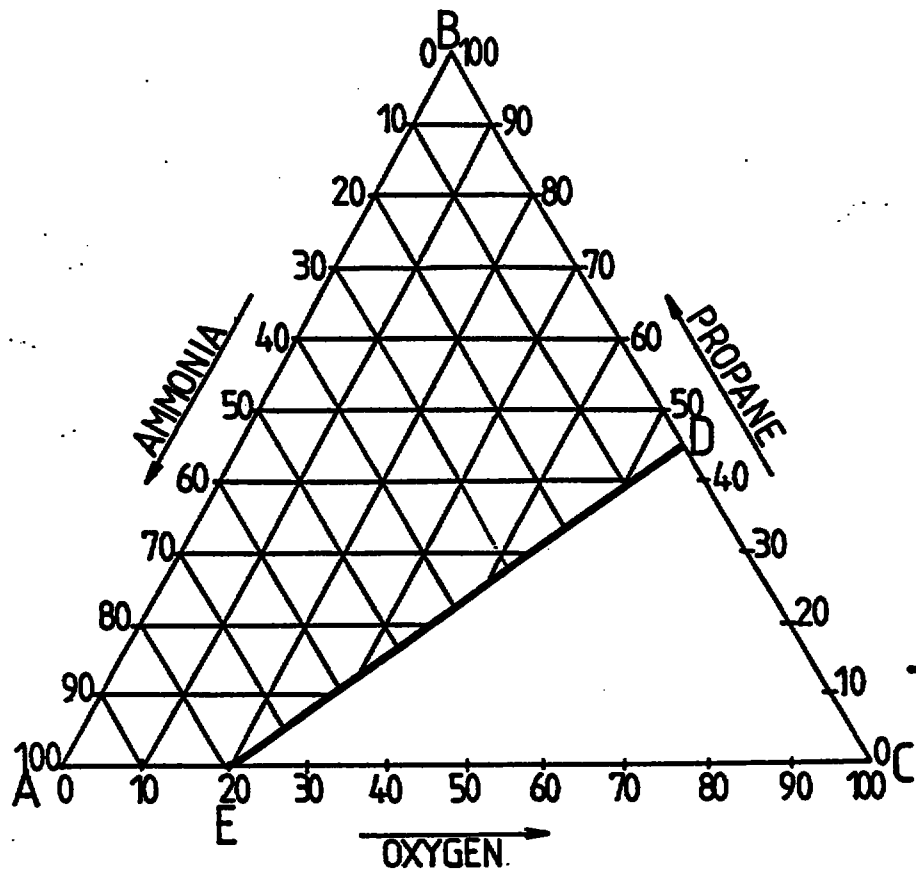


FIG. 1

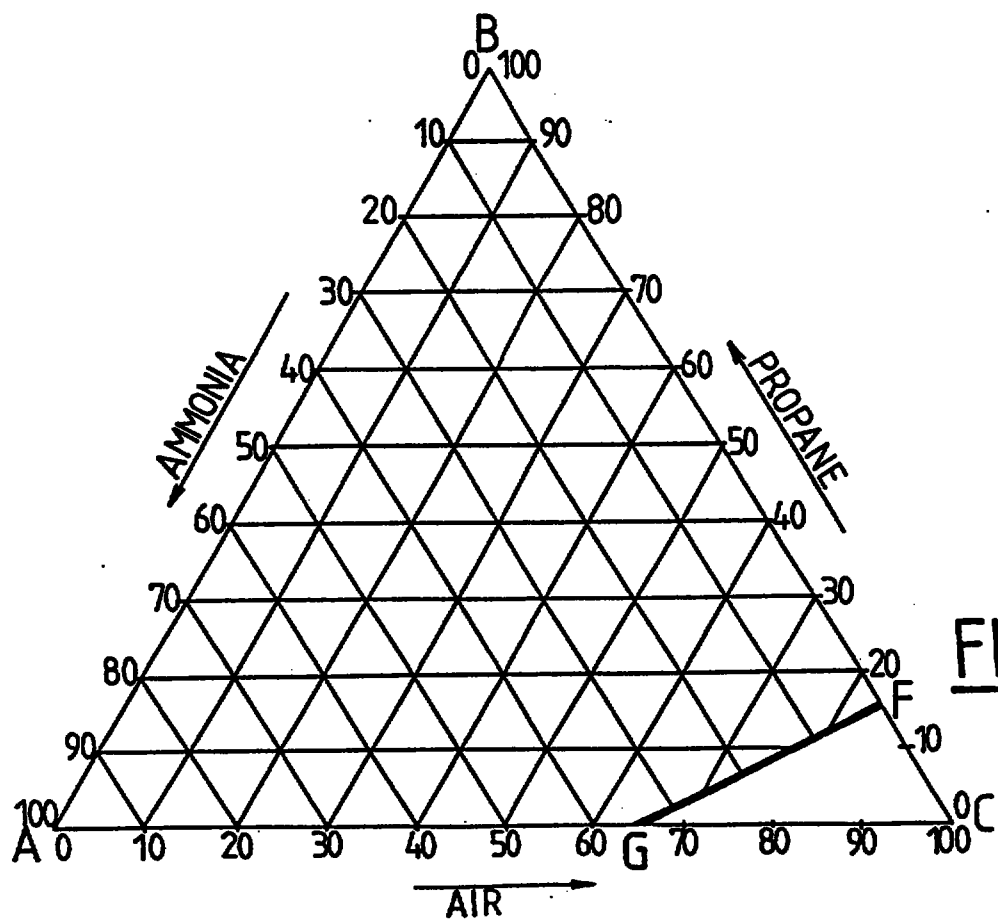
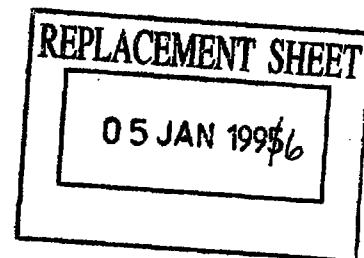


FIG. 2

**ABSTRACT****PROCESS FOR THE PREPARATION OF AMMOXIDATION CATALYSTS**

Process for the preparation of a mixed oxide, comprising vanadium, antimony and tin and corresponding to the empirical formula (I):



in which:

- a represents a whole or fractional number equal to or greater than 0.1,
- b represents a whole or fractional number equal to or greater than 0.5, and
- x represents a whole or fractional number determined by the oxidation states of the other elements, said mixed oxide exhibiting X-ray diffraction lines characteristic of a crystallographic phase of the SnO_2 rutile type, which process comprises:
 - dissolving vanadium, antimony and tin compounds in at least one saturated alcohol,
 - contacting the alcoholic solution thus obtained with an aqueous solution comprising an ammonium salt, in order to precipitate the mixed oxide, and
 - separating and calcining the mixed oxide.

Figure 1