

PROCESS FOR THE AMMOXIDATION OF SATURATED HYDROCARBONS

The present invention relates to a process for the ammoxidation of saturated hydrocarbons, that is to say the conversion of alkanes into a mixture
5 containing α, β -unsaturated nitriles.

It is well-known to those skilled in the art that very many proposals have been formulated regarding the ammoxidation of olefins and, in particular, that of propylene. However, although the saturated
10 hydrocarbons, which are more widely available, are more advantageous starting materials on the economic scale, it is also well-known that they do not have a comparable reactivity in this type of reaction to form especially α, β -unsaturated nitriles.

15 One of the difficulties encountered in the ammoxidation of saturated hydrocarbons resides in the necessity to be able to have available catalysts capable of dehydrogenating the saturated hydrocarbon under conditions which minimise or eliminate the
20 combustion of the ammonia and/or that of the hydrocarbon while ensuring a reasonable selectivity either for α, β -unsaturated nitrile (targeted product), for example for acrylonitrile starting from propane, or for enhanced value products (abovementioned nitrile and
25 olefin), for example, for acrylonitrile and propylene starting from propane.

It has already been proposed, in American

Patent No. 3,365,482, to ammoxidise, especially isobutane to methacrylonitrile, on a molybdenum-based catalyst deposited on eta-alumina, doped with antimony, at 508°C, starting from a gaseous mixture containing isobutane, air, ammonia and steam (1.0/4.5/1.0/12.5); the selectivity for methacrylonitrile reaches 49 % for a degree of conversion of the isobutane of 22 %.

Starting from a gaseous mixture of propane/air/ammonia/steam (1.0/4.7/0.67/12.8), with the same catalyst and at 550°C, the selectivity for acrylonitrile falls to 15 % for a degree of conversion of the propane of 29 %.

In "Chemistry Letters, 1989 (pp. 2173-2176)", writers tested, for the ammoxidation of propane in the vapour phase, multicomponent metal oxides containing molybdenum and bismuth and having a structure of the type of that of scheelite. It appears that, despite the relatively moderate temperatures used, the proportion of combustion products (CO, CO₂) is very high in all cases (at least 15 %) and that certain catalytic compositions tested have very little activity with respect to the desired reaction, while having a use under conditions which are in the explosive region or very near the said region.

It is obvious that the coproduction of large quantities of CO and CO₂ is undesirable on the industrial scale.

In addition, the use of reaction mixtures

which are in the explosive region is even less desirable on the industrial scale since the process is used in a stationary bed.

The patent US-A-4,760,159 describes a process for the ammoxidation of an alkane having 3 to 5 carbon atoms to an α,β -unsaturated nitrile having 3 to 5 carbon atoms, by reaction in the gas phase with ammonia and oxygen, in the presence of a solid catalyst having the formula $B_{1a}V_bL_1M_{1m}T_1O_x$, in which Bi, V, M (which is chosen from Mo, W, Cr, Ge and Sb) and O are always present.

Observation of the various embodiment examples shows that the best selectivities towards α,β -unsaturated nitrile are obtained with catalysts containing vanadium, bismuth and molybdenum and optionally another cation such as chromium, potassium, zinc, caesium or antimony. The only example of the use of a catalyst based on vanadium, bismuth and antimony having the formula $BiV_{0.7}Sb_{0.5}O_x$ deposited at 50 % on a silica/alumina mixture leads to yields of α,β -unsaturated nitrile which are markedly lower than with a catalyst containing molybdenum.

Additionally, this process also leads to the formation of a not insignificant quantity of oxides of carbon ($CO + CO_2$).

It thus remains desirable to have available a process for the ammoxidation of alkanes which makes it possible to obtain, with an appreciable selectivity, a

mixture of enhanced value products containing an α, β -unsaturated nitrile, in particular acrylonitrile, while reducing the losses in starting material especially as a result of the formation of oxides of carbon.

5 It would also be highly desirable to have available such a process in which the solid catalyst would be relatively simple to prepare and active in the absence of halogenated promoter and for gas mixtures which are not necessarily in the explosive region.

10 The subject of the present invention is thus a process for the ammoxidation of alkanes in the vapour phase in the presence of a solid catalyst comprising at least one active phase, characterised in that the said active phase corresponds to the following empirical
15 formula (I):



in which:

- a represents a whole or fractional number equal to or greater than 1,
- 20 - b represents a whole or fractional number equal to or greater than 0.01,
- x represents a whole or fractional number specified by the oxidation number of the other elements of the active phase.

25 Preferentially, in the formula (I) of the active phase described above:

- the symbol a represents a whole or fractional number up to 20 and is preferably between 1



and 10,

- the symbol b represents a whole or fractional number up to 20 and is preferably between 0.1 and 10.

5 The active phase used in the process of the invention can also comprise, besides the elements of the formula (I), iron and/or gallium and/or indium.

This variation of composition of the active phase can be represented by the empirical formula (II):



in which:

- a represents a whole or fractional number equal to or greater than 1,
- b represents a whole or fractional number
15 equal to or greater than 0.01,
- M represents an iron and/or gallium and/or indium atom,
- c represents a whole or fractional number equal to or greater than 0.1,
- x represents a whole or fractional number
20 specified by the oxidation number of the other elements of the active phase.

Preferentially, in the formula (II) of the active phase described above:

- 25 - the symbol a represents a whole or fractional number up to 20, [lacuna] between 1 and 10,
- the symbol b represents a whole or fractional number up to 20, preferably between 0.1 and



10,

- the symbol c represents a whole or fractional number up to 20, preferably between 0.5 and 10.

5 According to the present invention, acyclic saturated hydrocarbons 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 whose active phase has just been specified.

10 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
15 reactive gas (saturated hydrocarbon, ammonia, oxygen) can thus be diluted with an inert diluent and/or with steam. In this mixture, the content of steam can vary within wide limits, in particular from 0 to 50 % and, preferably, between 3 and 30 %. For a good
20 implementation of the process according to the invention, the content of reactive gas will be at least 3 % and preferably at least 20 %.

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

 The content of saturated hydrocarbon 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 %.

For a good implementation of the process according to the invention, the composition of the reaction mixture will be outside the explosive region.

- 5 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 the appended Figure 1.

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

- Segment DE marks off the ternary diagram into
20 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 advantageously be chosen.

- 25 Regarding the ammoxidation of propane in the presence of inert diluent gas(es) and/or of steam, it will be advisable to determine the composition of the ternary mixture (propane, oxygen and ammonia) in order

to situate it in 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
5 (propane, air and ammonia) will advantageously be chosen inside the quadrilateral ABFG which appears within diagram ABC represented in the appended Figure 2.

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

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

This second diagram will be used in the case
25 where the oxygen/diluent gas mixture corresponds to an oxygen content equivalent to that of the air (≈ 21 % 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 saturated hydrocarbon used can be of technical grade, it will not contain significant quantities of compounds containing ethylenic unsaturation. Thus, the propane involved will only contain trace amounts of propylene.

The process according to the invention is carried out in the form of a vapour phase reaction. Consequently, any device suitable for the carrying out of 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 fluidised bed.

The reaction temperature is generally 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. It is generally between 1 and 6 bar and, preferably, between 1 and 4 bar.

5 The gas flow rate is fixed such that the hourly volume rate is between 100 and 36,000 h⁻¹ and, preferably, between 200 and 20,000 h⁻¹.

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

10 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.

15 In the process according to the invention, the catalysts can be prepared or used in the following way.

An active phase consisting of a mixed oxide containing the elements V, Sb and Bi and, if
20 appropriate, the elements Fe and/or Ga and/or In is first synthesised.

This active phase can optionally be deposited on an inorganic oxide or mixed with the said inorganic oxide which is known to those skilled in the art, such
25 as, for example, alumina, silica, silica/alumina, zirconia, cerite, magnesia, titanium oxide or niobium oxide, by using various techniques known to those skilled in the art, such as impregnation or deposition

by "slurry".

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 the bulk form or in the particulate state; it can thus be used in the powder form or can be put into the form of, for example, balls, pellets, extrudates or crushed particles, according to various known techniques.

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

For an implementation of the process in a moving bed or in a fluidised bed, the catalytic phase is generally formed by spraying, drying and calcination.

The catalytic phase thus formed or in the powder form constitutes the catalyst according to the invention.

When the catalytic phase comprises the active phase deposited on an inorganic oxide or mixed with the said inorganic oxide, a variation of preparation can consist, in a single stage, in synthesising the active phase and depositing it on the inorganic oxide or mixing it with the said inorganic oxide.

In what follows, the synthesis of the active phase and its deposition on the inorganic oxide or its

mixing with the said inorganic oxide will be first described separately, but the description will also apply to the variation of synthesis of the active phase in the presence of the inorganic oxide.

5 The preparation of the active phases used in the process according to the invention can be achieved by various known techniques, such as mixing of suitable salts or oxides of the various metals in water or in another solvent, followed by evaporation to dryness, or
10 by precipitation by addition of a base such as aqueous ammonia or of an acid such as hydrochloric acid, or spraying of a suspension obtained after mixing the suitable salts.

 The most commonly employed suitable salts
15 contain anions or cations which can, for example, be decomposed by heat during the subsequent stages.

 Examples of suitable salts or oxides of vanadium which may be mentioned are: ammonium vanadate, vanadium oxyhalides such as VOCl_3 , VOCl_2 , $(\text{VO}_2)\text{Cl}$, VOCl ,
20 VOBr , VOBr_2 , VOBr_3 , VOF_3 and VOF_2 , vanadium halides such as VF_3 , VBr_3 , VCl_2 , VCl_3 , VCl_4 , VF_5 , VF_4 , VBr_2 and VI_2 , vanadyl sulphate, vanadyl acetylacetonate, meta-vanadic acid, hexacarbonylvanadium, vanadyl triisopropoxide, and vanadium oxides such as V_2O_5 , V_7O_{13} , VO , VO_2 , V_2O_3
25 and V_3O_7 .

 Examples of suitable salts or oxides of antimony which may be mentioned are antimony oxychloride, antimony halides such as SbBr_3 , SbCl_3 ,

SbF₃, SbI₃, SbCl₅, SbF₅ and SbI₅, antimony sulphate, antimony acetate, antimony tartrate, antimony ethoxide, antimony butoxide, the ethylene glycol derivative of antimony, antimony oxysulphate, or antimony oxides such
 5 as Sb₂O₃, Sb₂O₄ or Sb₂O₅.

Examples of suitable salts or oxides of bismuth which may be mentioned are: bismuth nitrate, bismuth oxyhalides such as BiOCl, BiOI, BiOBr and BiOF, bismuth halides such as BiCl₃, BiBr₃, BiF₃, BiI₃, BiCl₄
 10 and BiI₂, bismuth sulphate, bismuth acetate, bismuth propionate, bismuth oxalate, bismuth citrate, bismuth tartrate, bismuth lactate, bismuth benzoate, bismuth salicylate, bismuth oxycarbonate, bismuth oxynitrate, bismuth oxyperchlorate, or bismuth oxides such as Bi₂O₃
 15 or Bi₂O₅.

Examples of suitable salts or oxides of iron which may be mentioned are iron nitrate, iron perchlorate, iron oxychloride, iron halides such as FeCl₃, FeCl₂, FeBr₃, FeBr₂, FeF₃, FeF₂ and FeI₂, iron
 20 phosphate, iron sulphate, iron iodate, pentacarbonyl-iron, iron acetate, iron acetylacetonate, iron citrate, iron formate, iron gluconate, iron glycerophosphate, iron lactate, iron malate, iron methoxide, iron oleate, iron oxalate, iron tartrate, iron 2-ethylhexanoate, or
 25 iron oxides such as Fe₂O₃, Fe₃O₄ or FeO.

Examples of suitable salts or oxides of gallium which may be mentioned are gallium nitrate, gallium perchlorate, gallium oxychloride, gallium

halides such as GaCl_3 , GaCl_2 , GaBr_3 , GaF_3 or GaI_3 , gallium sulphate, gallium acetate, gallium acetylacetonate, gallium oxalate, or gallium oxides such as Ga_2O_3 or Ga_2O .

5 Examples of suitable salts or oxides of indium which may be mentioned are indium nitrate, indium perchlorate, indium halides such as InCl_3 , InCl_2 , InCl , InBr_3 , InBr_2 , InBr , InF_3 , InI_3 , InI_2 or InI , indium phosphate, indium sulphate, indium iodate,
10 indium acetate, indium acetylacetonate, indium methoxide, or indium oxides such as In_2O_3 , In_2O or InO .

The active phase is generally synthesised by the so-called evaporation method, in the following way: an aqueous suspension of the suitable salts or oxides
15 is prepared and the suspension is evaporated by heating between 20 and 100°C until a viscous paste is obtained, which is dried. The precursor thus obtained can then be ground and calcined between 200 and 1000°C. The active phase thus obtained can then, after cooling, be ground
20 so that its particle size does not exceed approximately 400 μm .

The precursor can also be obtained according to a variation comprising precipitation with addition, for example, of aqueous ammonia or of hydrochloric
25 acid, during or at the end of mixing of the salts or oxides. It is preferable to heat the suspension between 20 and 100°C to bring precipitation of the species to completion.

The suspension obtained can be evaporated according to the conditions described above, or filtered and washed. The paste or filtration cake, which are obtained respectively by evaporation or by
5 filtration, are then dried, ground and calcined according to the conditions described above in the context of the evaporation method, to give the active phase.

This active phase can optionally be deposited
10 on one or more inorganic oxides or can be mixed with the inorganic oxide(s) which are known to those skilled in the art. By way of examples of inorganic oxides capable of being suitable for the preparation of catalysts which can be used in the context of the
15 process according to the invention, there may be mentioned, in a nonlimiting way, alumina, silica, silica/alumina, zirconia, cerite, magnesia, titanium oxide or niobium oxide.

The deposition on these oxides or the mixing
20 with these inorganic oxides can be carried out by various known techniques, such as, for example, impregnation or deposition by "slurry".

The quantity of active phase, which can vary within wide limits, is in practice between 5 and 100 %
25 and preferably between 10 and 50 % by weight with respect to the combined active phase + inorganic oxide.

Another method commonly used in the context of the invention is the mixing of the inorganic oxide

with the suitable salts or oxides of the various metals of the active phase according to the conditions described above in the context of the preparation of the active phases. Once this mixture has been made, the precursor can be obtained by the so-called evaporation or precipitation methods, and then the paste or the filtration cake which are obtained are dried, ground and calcined according to the conditions described above in the context of the preparation of the active phases.

The active phase, alone or deposited on an inorganic oxide or mixed with an inorganic oxide such as those described above, constitute the catalytic phase.

The catalytic phases involved can be used in the bulk form or in the particulate state. These phases can therefore be used in the powder form or can be put, for example, into the form of balls, pellets, extrudates or crushed particles, according to various known techniques.

For an implementation of the process in a stationary bed, there may be mentioned, by way of examples of techniques which are possibly suitable for the preparation of the catalysts which can be used in the context of the process according to the invention: pelleting or coating on an inert support or on a ceramic or metal substrate of monolithic type.

The catalytic phases according to the

invention can, for example, be shaped by compression, so as to obtain pellets. These pellets can then be optionally 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 depending upon the acceptable pressure drop in the reactor.

The catalytic phases according to the invention 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 capable of being 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, carborandum, magnesia, magnesium silicate and diatomaceous earth. This support is preferably nonporous and can especially be based on refractory oxide in the 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 between 0.5 mm and 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,

the said substrate preferably being in the form of an inert and rigid structure of monolithic type comprising channels or ducts. Such supports are well-known and have been widely described in the literature. The
5 substrates used which are made of ceramic substances are especially those containing, as the main substance, cordierite, alumina, mullite, porcelain, and the carbides of boron or silicon.

This support can also be a metal substrate.
10 Such supports are well-known. Suitable metal substrates are especially those obtained from alloys of iron, nickel and chromium, or those obtained from alloys of iron, chromium, aluminium and cobalt, such as those known under the trade name Kanthal, or those obtained
15 from alloys of iron, chromium, aluminium and yttrium known under the trade mark Fecralloy. The metal can also be carbon steel or simple cast-iron.

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

Thus, certain catalysts, useful for an implementation of the process in a stationary bed, can
25 be obtained by coating ground, intermediate or finished, catalytic phases in a manner 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 between 70 and 150°C for at least 30 minutes and then introduced into an oven in order to
5 be calcined between 300 and 600°C, preferably between 450 and 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 fluidised bed can be
10 obtained by the technique, known per se, of drying by spraying in a preferably nonreducing atmosphere. By such an operation, followed if appropriate by calcination at a temperature of the order of 400 to 1100°C, powders are obtained which are spherical in
15 shape and have a diameter of between 5 and 700 μm . Powders consisting of at least 80 % by weight of particles whose sizes are between 5 and 200 μm are preferred in the context of use in a fluidised bed.

The catalytic phase thus used in the bulk
20 form or the particulate state constitutes the catalyst according to the invention.

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
25 containing dilute sulphuric acid in order to neutralise 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, CO₂. The acrylonitrile and hydrocyanic acid can then be separated from the acetonitrile by
 5 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 illustrate the present
 10 invention.

EXAMPLE 1 - Preparation of the catalyst (A₁)
according to the invention, of the
following empirical formula (III):
VSb_{3.5}Bi₂Ox/Al₂O₃ (25/75 % by weight)

15 (III)

a) A solution (a) of ammonium vanadate is prepared by dissolving 2.34 g of NH₄VO₃ in 400 cm³ of demineralised water, a solution (b) of bismuth nitrate is prepared by dissolving 19.4 g of
 20 Bi(NO₃)₃·5H₂O in 50 cm³ of demineralised water and 15 cm³ of concentrated nitric acid and a solution (c) of antimony chloride is prepared by dissolving 10.2 g of Sb₂O₃ in 250 cm³ of 1N hydrochloric acid. Solution (b) is added to solution (a) with
 25 stirring at approximately 70°C and then solution (c) is added. 47.3 g of Al₂O₃ are then added at approximately 90°C. The mixture is heated at 105°C for 6 h, evaporated to dryness, and the residue is

dried at 120°C for approximately 15 h and then calcined at 550°C for 10 h.

b) The product of formula (III) thus obtained is then compressed under a pressure of 4300 kg/cm².

5 Pellets are thus obtained with a diameter of 3 cm and a thickness of approximately 0.5 cm. These pellets are crushed to fragments with a particle size of between 0.3 and 0.8 cm constituting the catalyst A₁ in accordance with the invention.

10 EXAMPLE 2 - Preparation of the catalyst (A₂) according to the invention, of the following empirical formula:
VSb_{3.5}Bi₂Ox/Al₂O₃ (25/75 % by weight)
coated on clay

15 The product of formula (III) obtained in Stage a) of Example 1 is then used in the following way.

15 g of the said product prepared above are slowly dusted over 100 g of inert support composed of
20 clay balls with a mean diameter of 4.8 mm, placed beforehand in a rotary coating device and moistened with 10 % aqueous glucose solution; as soon as the balls are dry on the outside, a small quantity of the glucose solution is sprayed. The product of formula
25 (III) is then again dusted onto the balls. These operations are continued alternately until all the product of formula (III) has been coated on.

Drying is then carried out at 120°C for 2 hours and calcination is carried out for 6 hours at 480°C.

The catalyst A₂ thus obtained consists of 8.8 % by weight of VSb_{3.5}Bi₂Ox/Al₂O₃ (25/75 % by weight) coated on clay balls.

EXAMPLE 3 - Preparation of the catalyst (B)
according to the invention, of the
following empirical formula (IV):

10 VSb_{1.64}Bi_{0.9}Ox, coated on clay balls

A product of formula (IV) VSb_{1.64}Bi_{0.9}Ox is prepared according to the following procedure: a suspension of 19.3 g of V₂O₅ in 400 cm³ of demineralised water is prepared; 122.5 g of a 30 % solution of H₂O₂ in 15 water are added dropwise, with stirring, in three portions respectively of 49 g, 49 g and 24.5 g. A solution consisting of 92.7 g of Bi(NO₃)₃·5H₂O in 24 cm³ of concentrated HNO₃ and 61 cm³ of demineralised water is then added. 50.8 g of Sb₂O₃ are then added. The 20 mixture is brought to reflux, is allowed to evaporate to dryness, and the residue is dried at 120°C for approximately 15 h and then calcined at 650°C for 8 h.

The product of formula (IV) thus obtained has a specific surface, measured according to the B.E.T. 25 method, of 11 m²/g.

9 g of the product of formula (IV) thus prepared are slowly dusted over 66 g of inert support

composed of clay balls with a mean diameter of 4.8 mm, placed beforehand in a rotary coating device and moistened with 10 % aqueous glucose solution. As soon as the balls are dry on the outside, a small quantity of the glucose solution is sprayed. The product of formula (IV) is then again dusted onto the balls. These operations are continued alternately until all the said product has been coated on. Drying is then carried out at 120°C for 2 h and calcining at 480°C for 6 h.

The catalyst (B) thus obtained, in accordance with the invention, consists of 12 % by weight of $\text{VSb}_{1.64}\text{Bi}_{0.9}\text{Ox}$ coated on clay balls.

EXAMPLE 4 - Preparation of the catalyst (G)
according to the invention, of the
following empirical formula (V):

$\text{VSb}_{2.5}\text{Bi}_{0.5}\text{Ox}/\text{Al}_2\text{O}_3$ (50/50 % by weight)

A product of formula (V) $\text{VSb}_{2.5}\text{Bi}_{0.5}\text{Ox}$ is prepared according to the following procedure:

37.75 g of Sb_2O_5 are added with stirring to a hot solution of 10.92 g of ammonium vanadate in 300 cm³ of demineralised water. A solution of bismuth nitrate consisting of 22.6 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 58 cm³ of demineralised water and 8.7 cm³ of 65 % nitric acid is then added.

57 g of Al_2O_3 are then added. The mixture is evaporated to dryness, the product obtained is dried at 120°C for approximately 15 h, and then calcined at

290°C for 3 hours, at 425°C for 3 h and at 610°C for 3 h.

The product obtained is then compressed under a pressure of 4300 kg/cm². Pellets are thus obtained with a diameter of 3 cm and a thickness of approximately 0.5 cm. These pellets are then crushed to fragments with a particle size of between 0.3 cm and 0.8 cm.

The catalyst (G) thus obtained, in accordance with the invention, consists of 50/50 % by weight VSb_{2.5}Bi_{0.5}Ox/Al₂O₃.

EXAMPLE 5 - Preparation of the catalyst (H)
according to the invention, of the
following empirical formula (VI):

VSb_{3.5}Bi₂Fe₂Ox/Al₂O₃ (25/75 % by weight)

A product of formula (VI) VSb_{3.5}Bi₂Fe₂Ox is prepared according to the following procedure.

A solution of ammonium vanadate is prepared by dissolving 2.34 g of NH₄VO₃ in 350 cm³ of demineralised water. A solution of bismuth nitrate prepared by dissolving 19.4 g of Bi(NO₃)₃·5H₂O in 50 cm³ of demineralised water and 15 cm³ of concentrated nitric acid is added with stirring and at approximately 70°C and then a solution of iron nitrate, prepared by dissolving 16.2 g of Fe(NO₃)₃·9H₂O in 70 cm³ of demineralised water, is added with stirring at approximately 70°C. A hot suspension of 10.2 g of Sb₂O₃

in 210 cm³ of demineralised water and 21 cm³ of concentrated hydrochloric acid is then added, and 47.3 g of alumina are then added when the mixture is at a temperature of approximately 95°C.

5 The mixture is brought to reflux for 6 h and then evaporated to dryness, and the residue is dried at 120°C for approximately 15 h and calcined at 550°C for approximately 10 h.

10 The product obtained is then compressed under a pressure of 4300 kg/cm². Pellets are thus obtained with a diameter of 3 cm and a thickness of approximately 0.5 cm. These pellets are then crushed to fragments with a particle size of between 0.3 cm and 0.8 cm.

15 The catalyst (H) thus obtained, in accordance with the invention, consists of 25/75 % by weight VSb_{3.5}Bi₂Fe₂Ox/Al₂O₃.

EXAMPLE 6 - Preparation of the catalyst (J)
according to the invention, of the
 20 following empirical formula (VII):
VSb₅Bi₂Fe₂Ox/Al₂O₃ (25/75 % by weight)

A product of formula (VII) VSb₅Bi₂Fe₂Ox is prepared according to the following procedure.

25 A solution of ammonium vanadate is prepared by dissolving 2.34 g of NH₄VO₃ in 350 cm³ of demineralised water. A solution of bismuth nitrate prepared by dissolving 19.4 g of Bi(NO₃)₃·5H₂O in 50 cm³

of demineralised water and 15 cm³ of concentrated nitric acid is added with stirring and at approximately 70°C and then a solution of iron nitrate, prepared by dissolving 16.2 g of Fe(NO₃)₃·9H₂O in 70 cm³ of demineralised water, is added with stirring at approximately 70°C. A hot suspension of 14.57 g of Sb₂O₃ in 300 cm³ of demineralised water and 30 cm³ of concentrated hydrochloric acid is then added, and 47.3 g of alumina are then added when the mixture is at a temperature of approximately 90°C.

The mixture is brought to reflux for 6 h and then evaporated to dryness, and the residue is dried at 120°C for approximately 15 h and calcined at 550°C for approximately 10 h.

The product obtained is then compressed under a pressure of 4300 kg/cm². Pellets are thus obtained with a diameter of 3 cm and a thickness of approximately 0.5 cm. These pellets are then crushed to fragments with a particle size of between 0.3 cm and 0.8 cm.

The catalyst (J) thus obtained, in accordance with the invention, consists of 25/75 % by weight VSb₅Bi₂Fe₂Ox/Al₂O₃.

EXAMPLE 7 - Preparation of the catalyst (K)
according to the invention, of the
following empirical formula (VIII):
VSb₅Bi_{0.5}Fe₅Ox/Al₂O₃ (25/75 % by weight)

A product of formula (VIII) $\text{VSb}_5\text{Bi}_{0.5}\text{Fe}_5\text{O}_x$ is prepared according to the following procedure.

A solution of ammonium vanadate is prepared by dissolving 2.34 g of NH_4VO_3 in 350 cm³ of demineralised water. A solution of bismuth nitrate prepared by dissolving 4.85 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 20 cm³ of demineralised water and 3.75 cm³ of concentrated nitric acid is added with stirring and at approximately 70°C and then a solution of iron nitrate, prepared by dissolving 40.5 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 100 cm³ of demineralised water, is added with stirring at approximately 70°C. A hot suspension of 14.57 g of Sb_2O_3 in 300 cm³ of demineralised water and 30 cm³ of concentrated hydrochloric acid is then added, and 47.3 g of alumina are then added when the mixture is at a temperature of approximately 90°C.

The mixture is brought to reflux for 6 h and then evaporated to dryness, and the residue is dried at 120°C for approximately 15 h and calcined at 550°C for approximately 10 h.

The product obtained is then compressed under a pressure of 4300 kg/cm². Pellets are thus obtained with a diameter of 3 cm and a thickness of approximately 0.5 cm. These pellets are then crushed to fragments with a particle size of between 0.3 cm and 0.8 cm.

The catalyst (K) thus obtained, in accordance with the invention, consists of 25/75 % by weight

$\text{VSb}_5\text{Bi}_{0.5}\text{Fe}_5\text{Ox}/\text{Al}_2\text{O}_3$.

EXAMPLE 8 - Preparation of the catalyst (L)
according to the invention, of the
following empirical formula (IX):

5 $\text{VSb}_6\text{Bi}_6\text{FeOx}/\text{Al}_2\text{O}_3$ (25/75 % by weight)

A product of formula (IX) $\text{VSb}_6\text{Bi}_6\text{FeOx}$ is prepared according to the following procedure.

A solution of ammonium vanadate is prepared by dissolving 2.34 g of NH_4VO_3 in 350 cm^3 of
10 demineralised water. A solution of bismuth nitrate prepared by dissolving 58.2 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 120 cm^3 of demineralised water and 45 cm^3 of concentrated nitric acid is added with stirring and at approximately 70°C and then a solution of iron
15 nitrate, prepared by dissolving 8.1 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 20 cm^3 of demineralised water, is added with stirring at approximately 70°C. A hot suspension of 17.5 g of Sb_2O_3 in 180 cm^3 of demineralised water and 36 cm^3 of concentrated hydrochloric acid is then added,
20 and 47.3 g of alumina are then added when the mixture is at a temperature of approximately 90°C.

The mixture is brought to reflux for 6 h and then evaporated to dryness, and the residue is dried at 120°C for approximately 15 h and calcined at 550°C for
25 approximately 10 h.

The product obtained is then compressed under a pressure of 4300 kg/cm^2 . Pellets are thus obtained

with a diameter of 3 cm and a thickness of approximately 0.5 cm. These pellets are then crushed to fragments with a particle size of between 0.3 cm and 0.8 cm.

5 The catalyst (L) thus obtained, in accordance with the invention, consists of 25/75 % by weight $\text{VSb}_6\text{Bi}_6\text{FeOx}/\text{Al}_2\text{O}_3$.

COMPARATIVE TEST 1 - Preparation of the catalyst
(C) not in accordance with the
 10 invention, of the following
 empirical formula:

$\text{VSb}_{1.64}\text{Ox}$, coated on clay balls

A product of composition $\text{VSb}_{1.64}\text{Bi}_{0.9}\text{Ox}$ is prepared according to the following procedure. A
 15 suspension of 27.58 g of V_2O_5 in 400 cm^3 of demineralised water is prepared; 175 g of a 30 % solution of H_2O_2 in water are added dropwise, with stirring, in three portions respectively of 70 g, 70 g and 35 g. 72.56 g of Sb_2O_3 and then 200 cm^3 of
 20 demineralised water are then added. The mixture is brought to reflux and left to evaporate to dryness. The product obtained in then dried at 120°C for approximately 15 h, and then calcined at 650°C for 8 h.

The product thus obtained has a specific
 25 surface, measured according to the B.E.T. method, of 55 m^2/g .

7.5 g of the product $\text{VSb}_{1.64}\text{Ox}$ thus obtained

are slowly dusted over 50 g of inert support composed of clay balls with a mean diameter of 4.8 mm, placed beforehand in a rotary coating device and moistened with 10 % aqueous glucose solution. As soon as the balls are dry on the outside, a small quantity of the glucose solution is sprayed. The product $\text{VSb}_{1.64}\text{Ox}$ is then again dusted onto the balls. These operations are continued alternately until all the said product has been coated on. Drying is then carried out at 120°C for 2 h and calcining at 480°C for 6 h.

The catalyst (C) thus obtained, not in accordance with the invention, consists of 10.55 % by weight of $\text{VSb}_{1.64}\text{Ox}$ coated on clay balls.

COMPARATIVE TEST 2 - Preparation of the catalyst (D) not in accordance with the invention, of the following empirical formula:
 $\text{VSb}_{3.5}\text{Ox}/\text{Al}_2\text{O}_3$ (25/75 % by weight)

A product of composition $\text{VSb}_{3.5}\text{Ox}/\text{Al}_2\text{O}_3$ (25/75 % by weight) is prepared according to the following procedure. A solution (a) of ammonium vanadate is prepared by dissolving 2.34 g of NH_4VO_3 in 400 cm^3 of demineralised water and a suspension (b) of antimony chloride is prepared by dissolving 10.2 g of Sb_2O_3 in 21 cm^3 of hydrochloric acid and 230 cm^3 of demineralised [lacuna]. Suspension (b) is added to solution (a), and

then 47.3 g of Al_2O_3 are added, with stirring at approximately 80-90°C. The mixture is maintained at this temperature for 6 h, is evaporated to dryness, and the residue is dried at 120°C for approximately 15 h and is then calcined at 550°C for 10 h.

This product is then compressed under a pressure of 4300 kg/cm². Pellets are thus obtained with a diameter of 3 cm and a thickness of approximately 0.5 cm. These pellets are then crushed to fragments with a particle size of between 0.3 and 0.8 cm, constituting the catalyst (D), of composition $\text{VSb}_{3.5}\text{Ox}/\text{Al}_2\text{O}_3$ (25/75 % by weight), not in accordance with the invention.

COMPARATIVE TEST 3 -

Preparation of the catalyst

(E) not in accordance with the invention, of the following empirical formula:



(50/25/25 % by weight)

A product of composition $\text{BiV}_{0.7}\text{Sb}_{0.5}\text{Ox}/\text{SiO}_2/\text{Al}_2\text{O}_3$ (50/25/25 % by weight) is prepared according to the procedure described in the patent US 4,760,159.

10.78 g of Sb_2O_5 are added, with stirring, to a hot solution of ammonium vanadate (10.92 g of NH_4VO_3 in 300 cm³ of demineralised water). A solution of bismuth nitrate (64.7 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 150 cm³ of

demineralised water and 25 cm³ of 65 % nitric acid) is then added. 25 g of Al₂O₃ and 25 g of SiO₂ are then added. The mixture is left to evaporate to dryness, the product obtained is dried at 125°C for approximately 15 h, and is then calcined at 290°C for 3 h, at 425°C for 3 h and at 610°C for 3 h.

The product obtained is then compressed under a pressure of 4300 kg/cm². Pellets are thus obtained with a diameter of 3 cm and a thickness of approximately 0.5 cm. These pellets are then crushed to fragments with a particle size of between 0.3 and 0.8 cm, constituting the catalyst (E), of composition BiV_{0.7}Sb_{0.5}Ox/SiO₂/Al₂O₃ (50/25/25 % by weight), not in accordance with the invention.

15 COMPARATIVE TEST 4 - Preparation of the catalyst
 (F) not in accordance with the
 invention, of the following
 empirical formula:

Biv_{0.7}Sb_{0.5}Ox/Al₂O₃ (50/50 % by

20 weight)

A product of composition $\text{BiV}_{0.7}\text{Sb}_{0.5}\text{O}_x/\text{Al}_2\text{O}_3$ (50/50 % by weight) is prepared according to the procedure described in the patent US 4,760,159.

10.78 g of Sb_2O_5 are added, with stirring, to
25 a hot solution of ammonium vanadate (10.92 g of NH_4VO_3
in 300 cm^3 of demineralised water). A solution of
bismuth nitrate consisting of 64.7 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$,

150 cm³ of demineralised water and 25 cm³ of 65 % nitric acid is then added. 50 g of Al₂O₃ are then added. The mixture is left to evaporate to dryness, the product obtained is dried at 120°C for approximately 15 h, and
 5 is then calcined at 290°C for 3 h, at 425°C for 3 h and at 610°C for 3 h.

The product obtained is then compressed under a pressure of 4300 kg/cm². Pellets are thus obtained with a diameter of 3 cm and a thickness of
 10 approximately 0.5 cm. These pellets are then crushed to fragments with a particle size of between 0.3 and 0.8 cm, constituting the catalyst (F), of composition BiV_{0.7}Sb_{0.5}Ox/Al₂O₃ (50/50 % by weight), not in accordance with the invention.

15 COMPARATIVE TEST 5 - Preparation of the catalyst
(M) not in accordance with the
invention, of the following
empirical formula:
VSb_{3.5}Fe₂Ox/Al₂O₃ (25/75 % by
 20 weight)

a) A solution (a) of ammonium vanadate is prepared by dissolving 2.34 g of NH₄VO₃ on 400 cm³ of demineralised water, a solution (b) of iron nitrate is prepared by dissolving 16.2 g of
 25 Fe(NO₃)₃·9H₂O in 70 cm³ of demineralised water and a suspension (c) of antimony chloride is prepared by dissolving 10.2 g of Sb₂O₃ in 250 cm³ of 1N

hydrochloric acid. Solution (b) is added to solution (a) with stirring at approximately 70°C and then suspension (c) is added. 47.3 g of Al_2O_3 are then added at approximately 90°C. The mixture is maintained at 90°C for 6 h, evaporated to dryness, and the residue is dried at 120°C for approximately 15 h and then calcined at 550°C for 10 h.

b) The product thus obtained is then compressed under a pressure of 4300 kg/cm². Pellets are thus obtained with a diameter of 3 cm and a thickness of approximately 0.5 cm. These pellets are crushed to fragments with a particle size of between 0.3 and 0.8 cm constituting the catalyst M 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, steam and helium.

The total pressure of the reaction mixture, 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

36,000 h⁻¹, whose precise value will be shown for each Example.

Catalyst volume:

(catalytic phase + possible support): 25 cm³.

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

- The catalyst is brought to a temperature T₁, for example 300°C, and, after stabilising for 30 min at the
10 temperature T₁, 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
15 examined at the inlet temperature T₁ are calculated using relationships of the type:

 conversion of propane (% in moles) =
 converted propane/introduced propane
20 selectivity for acrylonitrile (% in moles) = propane converted to
 acrylonitrile/converted propane
- The catalyst is then brought from 300 to 550°C by increments of 20°C and the
25 conversion percentages and the selectivities are determined every
 40 min.

In the Examples below, the following

conventions are used:

	DCC ₃ H ₈	=	conversion of propane
	SACN	=	selectivity for acrylonitrile
5	SACN+C ₃ H ₆	=	selectivity towards acrylonitrile for propylene
	SCOX	=	selectivity for carbon monoxide and carbon dioxide
10	SAMMOX	=	selectivity for acetonitrile, hydrocyanic acid and other (amm)oxidation byproducts
15	SC ₁ C ₂	=	selectivity for methane, ethane and ethylene.

EXAMPLE 9 AND COMPARATIVE TEST 6

Measurement of the performance of the
catalysts (A₁) and (E).

20 The operating conditions used are the
following:

- Hourly volume rate = 1000 h⁻¹
- Total pressure = 1.3 bar
- Composition by volume of the reaction

25 mixture:

C ₃ H ₈	= 25 %
NH ₃	= 25 %

O₂ = 10 %

H₂O = 20 %

He = 20 %

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

Tests	Example 9				Comparative test 6			
	A ₁				E			
Catalyst used								
Temperature (in °C)	400	420	440	460	400	420	440	460
DCC ₃ H ₈ %	4	6	9	13	5	6	6	5
SACN %	37	49	60	67	22	27	27	19
SACN + C ₃ H ₈ %	58	70	77	79	65	66	68	66
SAMMOX %	42	30.5	23	21	35	31	27	29
SC ₁ C ₂ %	0	0	0	0	0	3	5	5
SCOX %	0	0	0	0	0	0	0	0

15

TABLE 1

EXAMPLE 10 AND COMPARATIVE TESTS 7 AND 8

Measurement of the performance of the
catalysts (A₁), (D) and (E).

The operating conditions used are the
20 following:

- Hourly volume rate = 1000 h⁻¹
- Total pressure = 1.3 bar
- Composition by volume of the reaction

mixture:

25

C₃H₈ = 48 %

NH₃ = 9 %

O₂ = 18 %

H₂O = 20 %

He = 5 %

30

The temperature conditions and the results

obtained are collated in Table 2 below.

Test	Example 10			Comparative test 7			Comparative test 8		
Catalyst used	A ₁			D			E		
Temperature (in °C)	400	420	440	400	420	440	400	420	440
DCC ₃ H ₈ %	5	10	14	18	17	19	9	9	11
SACN %	42	51	49	26	22	17	21	22	23
SACN + C ₃ H ₆ %	60	65	59	56	61	56	61	57	51
SAMMOX %	38	25	24	28	22	25	38	27	28
SC ₁ C ₂ %	0	1	3	1	0.3	3	1	3	4
SCOX %	1	9	15	15	17	17	0	13	18

TABLE 2

EXAMPLE 11 AND COMPARATIVE TEST 9

Measurement of the performance of the catalysts (A₁) and (E).

The operating conditions used are the following:

- Hourly volume rate = 1000 h⁻¹
- Total pressure = 1.3 bar
- Composition by volume of the reaction

mixture:

10	C ₃ H ₈	= 7.5 %
	NH ₃	= 15 %
	O ₂	= 15 %
	H ₂ O	= 20 %
	He	= 42.5 %

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

Tests	Example 11					Comparative test 9			
	A ₁					E			
Catalyst used									
Temperature (in °C)	400	420	440	460	480	400	420	440	460
20 DCC ₃ H ₈ %	1	5	10	19	30	12	21	28	32
SACN %	6	53	67	78	83	41	56	62	61
SACN + C ₃ H ₈ %	94	74	82	87	88	59	69	73	70
25 SAMMOX %	6	26	19	14	10	41	29	25	25
SC ₁ C ₂ %	0	0	0	0	0	0	1	2	4
SCOX %	0	0	0	0	1	0	0	0	0

TABLE 3

EXAMPLE 12 AND COMPARATIVE TEST 10

Measurement of the performance of the catalysts (B) and (C).

30 The operating conditions used are the

following:

- Hourly volume rate = 1000 h⁻¹
- Total pressure = 1.3 bar
- Composition by volume of the reaction

5 mixture:

C₃H₈ = 25 %

NH₃ = 10 %

O₂ = 25 %

H₂O = 20 %

10 He = 20 %

The temperature conditions and the results

obtained are collated in Table 4 below.

Tests	Example 12		Comparative test 10	
	B		C	
15 Catalyst used				
Temperature (in °C)	460	480	460	480
DCC ₃ H ₈ %	10	14	36	36
SACN %	45	40	48	23
SACN + C ₃ H ₈ %	73	67	54	61
20 SAMMOX %	23	22	36	23
SC ₁ C ₂ %	2	3	1	1
SCOX %	2	8	9	14

TABLE 4

EXAMPLE 13 AND COMPARATIVE TEST 11

25 Measurement of the performance of the catalysts (B) and (C).

The operating conditions used are the following:

- Hourly volume rate = 1000 h⁻¹
- 30 - Total pressure = 1.3 bar

- Composition by volume of the reaction

mixture:

	C_3H_8	= 7.5 %
	NH_3	= 15 %
5	O_2	= 15 %
	H_2O	= 20 %
	He	= 42.5 %

The temperature conditions and the results obtained are collated in Table 5 below.

10	Tests	Example 13		Comparative test 11	
	Catalyst used	B		C	
	Temperature (in °C)	460	480	460	480
	DCC_3H_8 %	11	14	23	28
15	SACN %	46	53	38	47
	SACN + C_3H_6 %	71	77	48	55
	SAMMOX %	24	77	48	42
	SC_1C_2 %	5	2	1	4
	SCOX %	0	0	2	0

TABLE 5

EXAMPLE 14

Measurement of the performance of the catalyst (A_2).

The operating conditions used are the following:

- Hourly volume rate = 1000 h^{-1}
- Total pressure = 1.3 bar
- Composition by volume of the reaction

mixture:

C_3H_8 = 48 %

NH_3 = 9 %

O_2 = 18 %

H_2O = 20 %

He = 5 %

The temperature conditions and the results obtained are collated in Table 6 below.

	460°C	480°C
DCC ₃ H ₈ %	2 %	3.5 %
SACN %	17 %	12 %
SACN + C ₃ H ₆ %	65 %	65 %
SAMMOX %	33 %	27 %
SC ₁ C ₂ %	2 %	8 %
SCOX %	0	0

TABLE 6

EXAMPLE 15 AND COMPARATIVE TEST 12

Measurement of the performance of the catalysts (G) and (F).

The operating conditions used are the following:

- Hourly volume rate = 1000 h⁻¹
- Total pressure = 1.3 bar
- Composition by volume of the reaction

mixture:

C_3H_8 = 7.5 %

NH_3 = 15 %

O_2 = 15 %

H_2O = 20 %

He = 42.5 %

The temperature conditions and the results obtained are collated in Table 7 below.

5	Tests	Example 15				Comparative test 12			
	Catalyst used	G				F			
10	Temperature (in °C)	360	380	400	440	360	380	400	440
	DCC ₂ H ₅ %	6	18	33	51	3	6	14	30
	SACN %	13	32	38	53	3	5	8	8
	SACN + C ₃ H ₆ %	46	46	47	60	15	14	13	10
15	SAMMOX %	50	45	33	26	85	85	87	88
	SC ₁ C ₂ %	0	0	0	0	0	0	0	2
	SCOX %	4	8	20	13	0	0	0	0

TABLE 7

EXAMPLE 16

Measurement of the performance of the catalyst (G).

The operating conditions used are the following:

- 25 - Hourly volume rate = 1000 h⁻¹
- Total pressure = 1.3 bar
- Composition by volume of the reaction

mixture:

	C ₃ H ₈	= 20 %
30	NH ₃	= 20 %
	O ₂	= 20 %
	H ₂ O	= 20 %
	He	= 20 %

The temperature conditions and the results obtained are collated in Table 8 below.

	360°C	380°C	400°C	420°C
DCC ₃ H ₈ %	23 %	26 %	26 %	26 %
SACN %	34 %	32 %	25 %	26 %
SACN + C ₃ H ₈ %	51 %	52 %	49 %	51 %
SAMMOX %	36 %	36 %	37 %	34 %
SC ₁ C ₂ %	0.1 %	0.3 %	0.2 %	0
SCOX %	13 %	12 %	14 %	15 %

TABLE 8

EXAMPLE 17 AND COMPARATIVE TEST 13

Measurement of the performance of the catalysts

(H) and (M).

The operating conditions used are the following:

- Hourly volume rate = 1000 h⁻¹
- Total pressure = 1.3 bar
- Composition by volume of the reaction

mixture:

C ₃ H ₈	= 7.5 %
NH ₃	= 15 %
O ₂	= 15 %
H ₂ O	= 20 %
He	= 42.5 %

The temperature conditions and the results obtained are collated in Table 9 below.

Tests	Example 17				Comparative test 13				
Catalyst used	H				M				
Temperature (in °C)	380	400	420	440	460	400	420	440	460
DCC ₃ H ₈ %	3	7	16	21	23	5	15	31	38
SACN %	47	73	85	90	81	34	66	74	66
SACN + C ₃ H ₈ %	68	84	89	93	83	65	78	81	75
SAMMOX %	32	16	11	6	7	33	18	18	10
SC ₁ C ₂ %	0	0	0	0	10	0	4	0	0
SCOX %	0	0	0	0	0	2	0	0	16

TABLE 9

EXAMPLE 18 AND COMPARATIVE TEST 14

Measurement of the performance of the catalysts (H) and (M).

The operating conditions used are the following:

- Hourly volume rate = 1000 h⁻¹
- Total pressure = 1.3 bar
- Composition by volume of the reaction

mixture:

10	C ₃ H ₈	= 48 %
	NH ₃	= .9 %
	O ₂	= 18 %
	H ₂ O	= 20 %
	He	= 5 %

15 The temperature conditions and the results obtained are collated in Table 10 below.

20	Tests	Example 18			Comparative test 14		
	Catalyst used	H			M		
	Temperature (in °C)	360	380	400	360	380	400
25	DCC ₃ H ₈ %	3	6	10	4	10	12
	SACN %	20	47	47	10	34	36
	SACN + C ₃ H ₈ %	37	63	58	43	60	63
30	SAMMOX %	63	37	30	56	39	36
	SC ₁ C ₂ %	0	0	1	0	0	0
	SCOX %	0	0	10	0	0	0

TABLE 10

EXAMPLE 19

Measurement of the performance of the catalyst (J).

The operating conditions used are the following:

- Hourly volume rate = 1000 h⁻¹
- Total pressure = 1.3 bar
- Composition by volume of the reaction

mixture:

5	C ₃ H ₈	= 7.5 %
	NH ₃	= 15 %
	O ₂	= 15 %
	H ₂ O	= 20 %
	He	= 42.5 %

10 The temperature conditions and the results obtained are collated in Table 11 below.

15	Temperature (in °C)	380	400	420	440	460
	DCC ₂ H ₄ %	3	7	14	22	39
	SACN %	23	48	80	89	82
	SACN + C ₃ H ₈ %	38	55	85	92	84
20	SAMMOX %	62	45	15	8	16
	SC ₁ C ₂ %	0	0	0	0	0
	SCOX %	0	0	0	0	0

TABLE 11

EXAMPLES 20 AND 21

25 Measurement of the performance of the catalyst (J).

The operating conditions used are the following:

- Hourly volume rate = 1000 h⁻¹
- Total pressure = 1.3 bar
- 30 - Composition by volume of the reaction

mixture:

Example 20:

35	C ₃ H ₈	= 20 %
	NH ₃	= 20 %
	O ₂	= 20 %

48

H₂O = 20 %

He = 20 %

Example 21:C₃H₈ = 48 %5 NH₃ = 9 %O₂ = 18 %H₂O = 20 %

He = 5 %

10 The temperature conditions and the results
obtained are collated in Table 12 below.

Temperature (in °C)	Example 20			Example 21	
	380	400	420	380	400
DCC ₃ H ₈ %	3	5	9	9	9
SACN %	30	56	52	31	32
SACN + C ₃ H ₈ %	41	65	59	42	44
SAMNOX %	54	35	41	58	26
SC ₁ C ₂ %	5	0	0	0	1
SCOX %	0	0	0	0	28

TABLE 1225 EXAMPLE 22

Measurement of the performance of the catalyst
(K).

The operating conditions used are the following:

- Hourly volume rate = 1000 h⁻¹
- 30 - Total pressure = 1.3 bar
- Composition by volume of the reaction
mixture:

C₃H₈ = 7.5 %NH₃ = 15 %35 O₂ = 15 %H₂O = 20 %

He = 42.5 %

	Temperature (in °C)	360	380	400	410
5	DCC ₃ H ₈ %	3	7	21	23
	SACN %	25	53	54	57
	SACN + C ₃ H ₆ %	39	65	60	65
10	SAMMOX %	61	35	40	35
	SC ₁ C ₂ %	0	0	0	0
	SCOX %	0	0	0	0

TABLE 14**EXAMPLE 24**

15 Measurement of the performance of the catalyst
(K).

The operating conditions used are the following:

- Hourly volume rate = 1000 h⁻¹
- Total pressure = 1.3 bar
- 20 - Composition by volume of the reaction
mixture:

	C ₃ H ₈	= 48 %
	NH ₃	= 9 %
	O ₂	= 18 %
25	H ₂ O	= 20 %
	He	= 5 %

The temperature conditions and the results
obtained are collated in Table 15 below.

The temperature conditions and the results obtained are collated in Table 13 below.

Temperature (in °C)	360	380	400	420	440	460
DCC ₂ H ₃ %	4	11	18	29	39	40
SACN %	31	56	75	84	77	71
SACN + C ₃ H ₆ %	43	61	80	87	80	74
SAMMOX %	57	39	20	10	14	21
SC ₁ C ₂ %	0	0	0	0	0	1
SCOX %	0	0	0	3	6	4

TABLE 13

EXAMPLE 23

Measurement of the performance of the catalyst (K).

The operating conditions used are the following:

- Hourly volume rate = 1000 h⁻¹
- Total pressure = 1.3 bar
- Composition by volume of the reaction mixture:

C ₃ H ₈	= 20 %
NH ₃	= 20 %
O ₂	= 20 %
H ₂ O	= 20 %
He	= 20 %

The temperature conditions and the results obtained are collated in Table 14 below.

Temperature (in °C)	360	380	390	400	410
DCC ₃ H ₈ %	6	9	11	12	12
SACN %	19	28	32	42	46
SACN + C ₃ H ₆ %	37	49	48	56	60
SAMMOX %	63	51	40	28	24
SC ₁ C ₂ %	0	0	0	1	0
SCOX %	0	0	12	15	16

TABLE 15

EXAMPLE 25

Measurement of the performance of the catalyst

(L).

The operating conditions used are the following: .

- Hourly volume rate = 1000 h⁻¹
- Total pressure = 1.3 bar
- Composition by volume of the reaction

mixture:

C₃H₈ = 7.5 %

NH₃ = 15 %

O₂ = 15 %

H₂O = 20 %

He = 42.5 %

The temperature conditions and the results obtained are collated in Table 16 below.

Temperature (in °C)	380	400	420	440	460	470
DCC ₃ H ₈ %	1	3	5	7	16	29
SACN %	18	33	53	70	84	90
SACN + C ₃ H ₆ %	18	42	61	76	86	91
SAMMOX %	82	58	39	24	14	7
SC ₁ C ₂ %	0	0	0	0	0	2
SCOX %	0	0	0	0	0	0

TABLE 16

EXAMPLE 26

Measurement of the performance of the catalyst

(L).

The operating conditions used are the following:

- 5 - Hourly volume rate = 1000 h⁻¹
 - Total pressure = 1.3 bar
 - Composition by volume of the reaction

mixture:

	C_3H_8	= 20 %
10	NH_3	= 20 %
	O_2	= 20 %
	H_2O	= 20 %
	He	= 20 %

The temperature conditions and the results

15 obtained are collated in Table 17 below.

	Temperature (in °C)	380	400	420	440
20	DCC ₃ H ₈ %	2	4	8	13
	SACN %	14	28	50	72
	SACN + C ₃ H ₈ %	17	31	53	74
25	SAMMOX %	83	69	47	26
	SC ₁ C ₂ %	0	0	0	0
	SCOX %	0	0	0	0

TABLE 17

EXAMPLE 27

Measurement of the performance of the catalyst

30 (L).

The operating conditions used are the following:

- Hourly volume rate = 1000 h⁻¹
 - Total pressure = 1.3 bar
 - Composition by volume of the reaction

35 mixture:

$\text{C}_3\text{H}_8 = 48 \%$
 $\text{NH}_3 = 9 \%$
 $\text{O}_2 = 18 \%$
 $\text{H}_2\text{O} = 20 \%$
 $\text{He} = 5 \%$

The temperature conditions and the results obtained are collated in Table 18 below.

Temperature (in °C)	380	400	420
DCC ₃ H ₈ %	3	5	11
SACN %	18	40	68
SACN + C ₃ H ₈ %	25	47	73
SAMMOX %	75	53	26
SC ₁ C ₂ %	0	0	1
SCOX %	0	0	0

TABLE 18

CLAIMS

1. Process for the ammoxidation of alkanes
in the vapour phase in the presence of a solid catalyst
comprising at least one active phase, characterised in
5 that the said active phase corresponds to the following
empirical formula (I):



in which:

- a represents a whole or fractional number
10 equal to or greater than 1,
- b represents a whole or fractional number
equal to or greater than 0.01,
- x represents a whole or fractional number
15 specified by the oxidation number of the
other elements of the active phase.

2. Process according to Claim 1,
characterised in that the said active phase corresponds
to the formula (I) in which:

- the symbol a represents a whole or fractional
20 number up to 20 and is preferably between 1
and 10,
- the symbol b represents a whole or fractional
number up to 20 and is preferably from 0.1 to
10.

25 3. Process for the ammoxidation of alkanes
in the vapour phase in the presence of a solid catalyst
comprising at least one active phase, characterised in
that the said active phase corresponds to the following





empirical formula (II):



in which:

- a represents a whole or fractional number equal to or greater than 1,
- b represents a whole or fractional number equal to or greater than 0.01,
- M represents an iron and/or gallium and/or indium atom,
- c represents a whole or fractional number equal to or greater than 0.1,
- x represents a whole or fractional number specified by the oxidation number of the other elements of the active phase.

4. Process according to Claim 3, characterised in that the said active phase corresponds to the formula (II) in which:

- the symbol a represents a whole or fractional number up to 20, preferably between 1 and 10,
- the symbol b represents a whole or fractional number up to 20, preferably between 0.1 and 10,
- the symbol c represents a whole or fractional number up to 20, preferably between 0.5 and 10.

5. Process according to one of Claims 1 to 4, characterised in that the alkane is propane.

6. Process according to one of Claims 1 to



5, characterised in that the reaction is carried out in the presence of steam.

7. Process according to one of Claims 1 to 6, characterised in that the reaction temperature is between 300°C and 550°C and preferably between 400°C and 500°C.

8. Process according to one of Claims 1 to 7, characterised in that the total pressure is between 1 and 6 bar.

10 9. Process according to one of Claims 1 to 8, characterised in that the hourly volume rate is between 100 and 36,000 h⁻¹.

15 10. Process according to one of Claims 1 to 9, characterised in that, in the reactive gas (mixture of saturated hydrocarbon, ammonia and oxygen), the content of saturated hydrocarbon is between 5 and 70 %, the content of ammonia is between 3 and 50 % and the content of oxygen is between 3 and 45 %.

20 11. Process according to one of Claims 1 to 10, characterised in that the composition of the gaseous mixture is outside the explosive region.

25 12. Process according to one of Claims 1 to 11, characterised in that the solid catalyst contains, besides the said active phase, at least one inorganic oxide.

13. Process according to Claim 12, characterised in that the inorganic oxide is chosen from alumina, silica, silica/alumina, zirconia, cerite,



magnesia, titanium oxide, niobium oxide and their mixtures.

14. Process according to one of Claims 1 to 11, characterised in that the solid catalyst contains, besides the said active phase, an inert support or a ceramic or metal substrate of monolithic type.

15. Process according to either of Claims 12 and 13, characterised in that the solid catalyst also contains an inert support or a ceramic or metal substrate of monolithic type.

16. Process according to either of Claims 12 and 13, characterised in that the active phase of the catalyst represents from 5 % to 100 % by weight of the weight of the said catalyst and preferably from 10 % to 50 % weight/weight.

17. Process according to either of Claims 14 and 15, characterised in that the active phase or the catalytic phase represents from 1 % to 50 % by weight of the weight of the catalyst and preferably from 5 % to 35 % weight/weight.

PROCESS FOR THE AMMOXIDATION OF SATURATED HYDROCARBONS

ABSTRACT

The present invention relates to a process for the ammoxidation of saturated hydrocarbons, that is to say the conversion of alkanes to a mixture containing α, β -unsaturated nitriles.

More particularly, the subject of the present invention is a process for the ammoxidation of alkanes in the vapour phase in the presence of a solid catalyst whose active phase contains vanadium, antimony, bismuth and oxygen.

The present invention is more particularly suitable for the ammoxidation of propane to a mixture containing acrylonitrile and propylene.

1 / 1

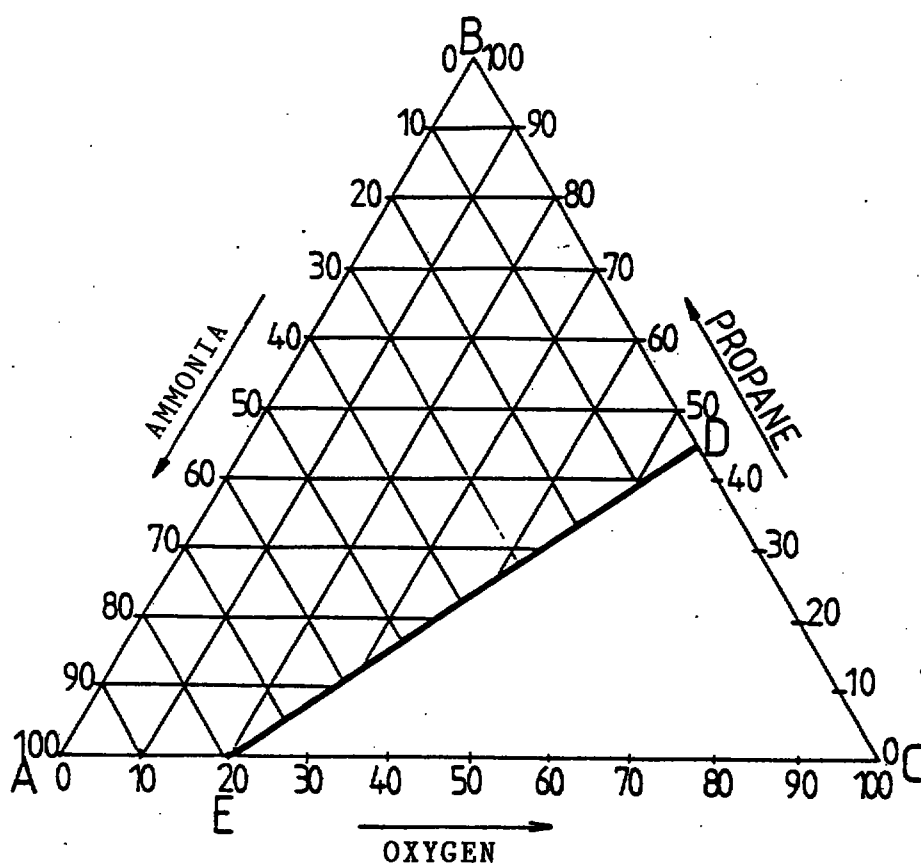


FIG. 1

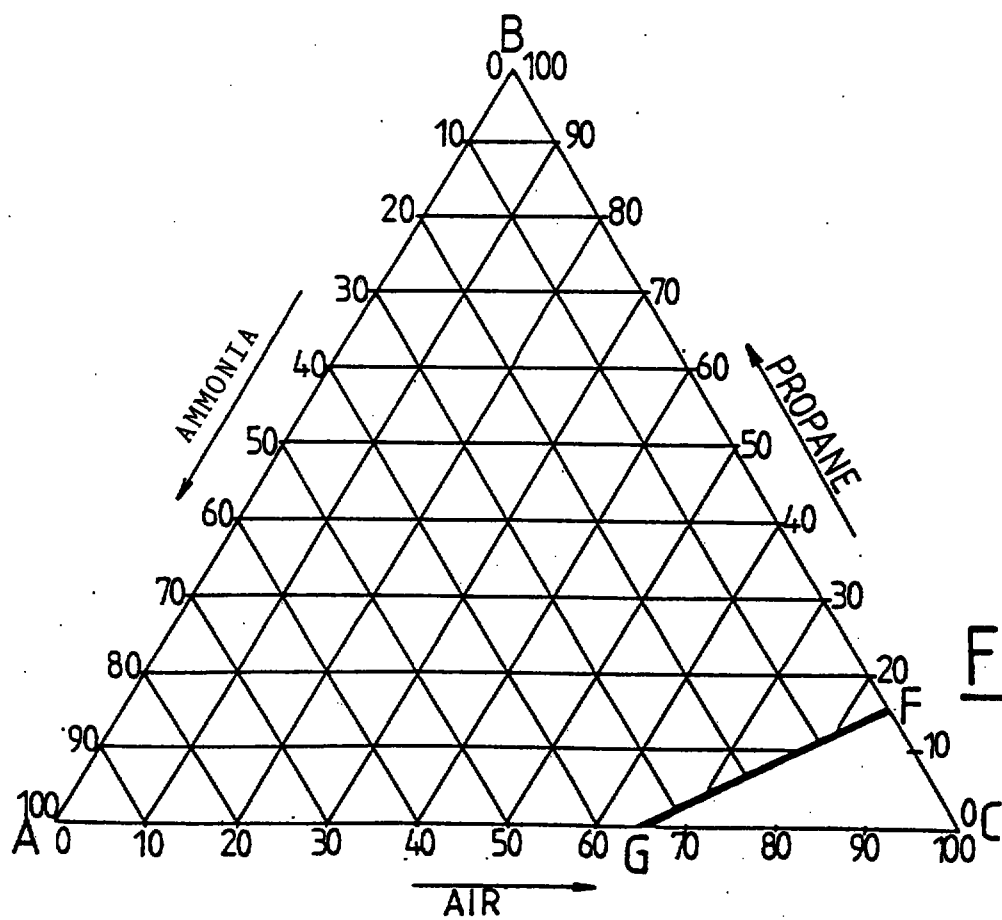


FIG. 2

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possible to obtain, with an appreciable selectivity, a mixture of enhanced value products containing an α , β -unsaturated nitrile, in particular acrylonitrile, while reducing the losses in starting material especially as a result of the formation of oxides of carbon.

It would also be highly desirable to have available such a process in which the solid catalyst would be relatively simple to prepare and active in the absence of halogenated promoter and for gas mixtures which are not necessarily in the explosive region.

The present invention therefore provides a process for the ammoxidation of alkanes in the vapour phase in the presence of a solid catalyst consisting essentially of an active phase corresponding to the following empirical formula (I):



in which:

- a represents a whole or fractional number equal to or greater than 1,
- b represents a whole or fractional number equal to or greater than 0.01,
- x represents a whole or fractional number specified by the oxidation number of the other elements of the active phase.

Preferentially, in the formula (I) of the active phase described above:

- the symbol a represents a whole or fractional number up to 20 and is preferably between 1 and 10,
- the symbol b represents a whole or fractional



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number up to 20 and is preferably between 0.1 and 10.

The active phase used in the process of the invention can also comprise, besides the elements of the
5 formula (I), iron and/or gallium and/or indium.

Thus, the present invention also provides a process for the ammoxidation of alkanes in the vapour phase in the presence of a solid catalyst consisting essentially of an active phase corresponding to the following empirical
10 formula (II):



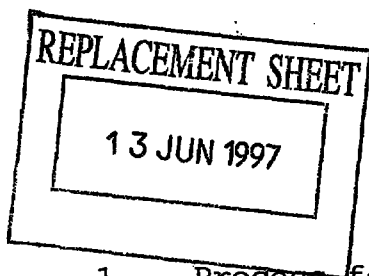
in which:

- 15 - a represents a whole or fractional number equal to or greater than 1,
 - b represents a whole or fractional number equal to or greater than 0.01,
 - M represents an iron and/or gallium and/or
20 indium atom,
 - c represents a whole or fractional number equal to or greater than 0.1,
 - x represents a whole or fractional number specified by the oxidation number of the other
25 elements of the active phase.

Preferentially, in the formula (II) of the active phase described above:

- the symbol a represents a whole or fractional
 number up to 20, preferably between 1 and 10,
30 - the symbol b represents a whole or fractional





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CLAIMS



1. Process for the ammoxidation of alkanes in the vapour phase in the presence of a solid catalyst consisting essentially of an active phase corresponding to the following empirical formula (I):



in which:

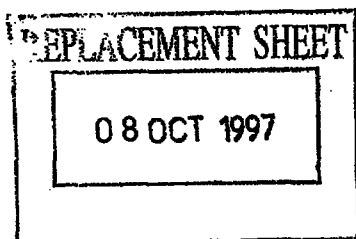
- a represents a whole or fractional number equal to or greater than 1,
- b represents a whole or fractional number equal to or greater than 0.01,
- x represents a whole or fractional number specified by the oxidation number of the other elements of the active phase.

2. Process according to claim 1, characterised in that the said active phase corresponds to the formula (I) in which:

- the symbol a represents a whole or fractional number up to 20 and is preferably between 1 and 10,
- the symbol b represents a whole or fractional number up to 20 and is preferably from 0.1 to 10.

3. Process for the ammoxidation of alkanes in the vapour phase in the presence of a solid catalyst consisting essentially of an active phase corresponding to the following





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mixture of enhanced value products containing an α , β -unsaturated nitrile, in particular acrylonitrile, while reducing the losses in starting material especially as a
5 result of the formation of oxides of carbon.

It would also be highly desirable to have available such a process in which the solid catalyst would be relatively simple to prepare and active in the absence of halogenated promoter and for gas mixtures which are not
10 necessarily in the explosive region.

The present invention therefore provides a process for the ammoxidation of alkanes in the vapour phase in the presence of a solid catalyst consisting essentially of an active phase corresponding to the following empirical
15 formula (I):

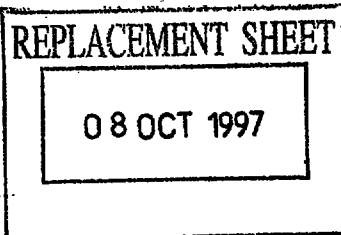


in which:

- 20 - a represents a whole or fractional number equal to or greater than 1,
 - b represents a whole or fractional number equal to or greater than 0.01,
 - x represents a whole or fractional number
25 specified by the oxidation number of the other elements of the active phase.

Preferentially, in the formula (I) of the active phase described above:

- 30 - the symbol a represents a whole or fractional number up to 20 and is preferably between 1 and 10,
 the symbol b represents a whole or fractional



- 5 -

number up to 20 and is preferably between 0.1 and 10.

The active phase used in the process of the invention can also comprise, besides the elements of the formula (I), iron and/or gallium and/or indium.

Thus, the present invention also provides a process for the ammoxidation of alkanes in the vapour phase in the presence of a solid catalyst consisting essentially of an active phase corresponding to the following empirical formula (II):



in which:

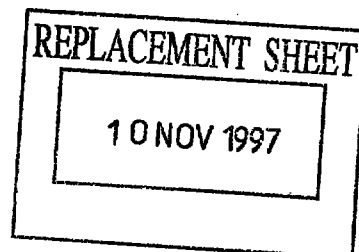
- a represents a whole or fractional number equal to or greater than 1,
- b represents a whole or fractional number equal to or greater than 0.01,
- M represents an iron and/or gallium and/or indium atom,
- c represents a whole or fractional number equal to or greater than 0.1,
- x represents a whole or fractional number specified by the oxidation number of the other elements of the active phase.

Preferentially, in the formula (II) of the active phase described above:

- the symbol a represents a whole or fractional number up to 20, preferably between 1 and 10,
- the symbol b represents a whole or fractional number up to 20, preferably between 0.1 and



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CLAIMS

1. Process for the ammoxidation of alkanes in the vapour phase in the presence of a solid catalyst consisting essentially of an active phase corresponding to the following empirical formula (I):



in which:

- a represents a whole or fractional number equal to or greater than 1,
- b represents a whole or fractional number equal to or greater than 0.01,
- x represents a whole or fractional number specified by the oxidation number of the other elements of the active phase.

2. Process according to claim 1, characterised in that the said active phase corresponds to the formula (I) in which:

- the symbol a represents a whole or fractional number up to 20 and is preferably between 1 and 10,
- the symbol b represents a whole or fractional number up to 20 and is preferably from 0.1 to 10.

3. Process for the ammoxidation of alkanes in the vapour phase in the presence of a solid catalyst consisting essentially of an active phase corresponding to the following