

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
5 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
10 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)", the writers tested, for the ammoxidation of propane in
15 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)
20 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, despite being used under conditions which are in the explosive region or very near the said region.

25 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.

Patent US-A-5,008,427 describes a process for
5 the ammoxidation of propane or isobutane to α,β -unsaturated mononitrile by reaction in the vapour phase with oxygen and ammonia in the presence of a catalyst comprising vanadium, antimony, oxygen and titanium and/or tin and/or iron and/or chromium and/or
10 gallium and optionally one or more other elements chosen from 23 very diverse metals. Apart from the composition of the catalyst, the main characteristics of the process described in this document are the calcination temperature of the catalyst, which must be
15 at least 780°C, and the alkane/ammonia (from 2.5 to 16) and alkane/oxygen (from 1 to 10) molar ratios.

This process would make it possible to obtain good productivity with regard to unsaturated nitrile with a catalyst which does not agglomerate.

20 However, this document, which is thus essentially centred on operating conditions such as calcination temperature or reactant ratios, does not make it possible more particularly to select compositions containing an active phase which makes
25 possible good selectivity for unsaturated nitrile.

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 - M represents an iron and/or gallium and/or indium atom,
- b represents a whole or fractional number equal to or greater than 0.5,
- 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:

- 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 1 and 10.

Among the metals represented by M in the formula (I) of the active phase, iron is generally preferred as this enables excellent selectivities for unsaturated nitrile and for ethylenic hydrocarbon to be obtained, while having good activity.

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.

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 (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 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 can vary within wide limits.

5 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
10 according to the invention, the composition of the reaction 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
15 quadrilateral ABDE which appears in the ternary diagram ABC represented in the appended Figure 1.

In this ternary diagram, segment AB represents the ammonia content from 100 % to 0 %; segment BC represents the propane content from 100 to
20 0 %; segment CA represents the oxygen content from 100 to 0 %. Point D, situated on segment BC, corresponds to 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
25 system (ammonia/O₂).

Segment DE marks off the ternary diagram into 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.

5 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.

10 Regarding the ammoxidation of propane by means of air as the oxygen source, the composition (propane, air and ammonia) will advantageously be chosen inside the quadrilateral ABFG which appears within diagram ABC represented in the appended Figure
15 2.

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

25 Segment FG marks off the ternary diagram into 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 advantageously be chosen.

This second diagram will be used in the case where the oxygen/diluent gas mixture corresponds to an
5 oxygen content equivalent to that of the air ($\approx 21\%$ 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
10 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.

15 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
20 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
25 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 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 fluidised bed.

5 The reaction temperature is generally between 300°C and 550°C and, preferably, between 350°C and 500°C.

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

 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.

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

 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
20 and the various other parameters of the reaction taking into account their production objectives.

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

25 An active phase consisting of a mixed oxide containing the elements V, Sb and 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 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 existing 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 variant 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.

5 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 variant of synthesis of the active phase
10 in the presence of the inorganic oxide.

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 elements in water or in
15 another solvent, followed by evaporation to dryness, or 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.

20 The most commonly employed suitable salts contain anions and 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,
25 vanadium oxyhalides such as VOCl_3 , VOCl_2 , $(\text{VO}_2)\text{Cl}$, VOCl , 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 and V_3O_7 .

Examples of suitable salts or oxides of antimony which may be mentioned are antimony oxychloride, antimony halides such as $SbBr_3$, $SbCl_3$, SbF_3 , SbI_3 , $SbCl_5$, SbF_5 and SbI_5 , antimony sulphate, antimony acetate, antimony tartrate, antimony ethoxide, antimony butoxide, the ethylene glycol derivative of antimony, antimony oxysulphate, or antimony oxides such as Sb_2O_3 , Sb_2O_4 or Sb_2O_5 .

Examples of suitable salts or oxides of iron which may be mentioned are iron nitrate, iron perchlorate, iron oxychloride, iron halides such as $FeCl_3$, $FeCl_2$, $FeBr_3$, $FeBr_2$, FeF_3 , FeF_2 and FeI_2 , iron 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 iron oxides such as Fe_2O_3 , Fe_3O_4 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 .

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 ,
5 indium phosphate, indium sulphate, indium iodate, 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:
10 an aqueous suspension of the suitable salts or oxides 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
15 phase thus obtained can then, after cooling, be ground so that its particle size does not exceed approximately 400 μm .

The precursor can also be obtained according to a variant comprising precipitation with addition,
20 for example, of aqueous ammonia or of hydrochloric 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.

25 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

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.

5 This active phase can optionally be deposited 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
10 catalysts which can be used in the context of the 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.

15 The deposition on these oxides or the mixing 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
20 within wide limits, is in practice between 5 and 100 % 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
25 with the suitable salts or oxides of the various elements 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, constitutes 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, carborundum, 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

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.

5 This support can also be a metal substrate. 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
10 known under the trade name Kanthal, or those obtained 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
15 of catalytic phase, which can vary within wide limits, is in practice between 1 and 50 % and preferably between 3 and 35 % by weight with respect to the combined support + catalytic phase.

 Thus, certain catalysts, useful for an
20 implementation of the process in a stationary bed, can 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
25 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

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 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 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 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 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, 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.

5 The examples below illustrate the present
invention.

EXAMPLE 1 - Preparation of the catalyst (A₁)
according to the invention, of the
following empirical formula (II):

10 V_{Sb_{3.5}}Fe₂Ox/Al₂O₃ (25/75 % by weight)
(II)

- 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 iron
15 nitrate is prepared by dissolving 16.2 g of
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
20 solution (a) with stirring at approximately 70°C
and then suspension (c) is added. 47.3 g of Al₂O₃
are then added at approximately 90°C. The mixture
is held at 90°C for 6 h, evaporated to dryness,
and the residue is dried at 120°C for
25 approximately 15 h and then calcined at 550°C for
10 h.
- b) The product of formula (II) 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 A_1 in accordance with the invention.

EXAMPLE 2 - Preparation of the catalyst (A_2) according to the invention, of the following empirical formula:
 $VSb_{3.5}Fe_2Ox/Al_2O_3$ (25/75 % by weight)
coated on clay

The product of formula (II) 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 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 (II) is then again dusted onto the balls. These operations are continued alternately until all the product of formula (II) 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 A_2 thus obtained consists of 10.4 % by weight of $VSb_{3.5}Fe_2Ox/Al_2O_3$ (25/75 % by

weight) coated on clay balls.

EXAMPLE 3 - Preparation of the catalyst (B₁)
according to the invention, of the
following empirical formula (III):

5 **VSb_{3.5}Ga₂Ox/Al₂O₃ (25/75 % by weight)**

- a) The product of formula (III) VSb_{3.5}Ga₂Ox/Al₂O₃ is prepared in the following way: a solution a) of ammonium vanadate is prepared by dissolving 2.34 g of NH₄VO₃ in 400 cm³ of demineralised water, a
 10 solution b) of gallium nitrate is prepared by dissolving 10.2 g of Ga(NO₃)₃ in 50 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.
 15 Solution b) is added to solution a) with stirring at approximately 80°C, and then suspension c) is added. 47.3 g of Al₂O₃ are then added at approximately 90°C. The mixture is heated at 105°C for 6 hours and evaporated to dryness, and the
 20 residue is dried at 120°C for approximately 15 hours and then calcined at 550°C for 10 hours.
- b) The product of formula III thus prepared in a) is then compressed under a pressure of 4300 kg/cm². Pellets are thus obtained with a diameter of 3 cm
 25 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 constituting the catalyst B₁ in accordance with

the invention.

EXAMPLE 4 - Preparation of the catalyst (B₂)
according to the invention, of the
empirical formula:

5 **VSb_{3.5}Ga₂Ox/Al₂O₃ (25/75% by weight)**
coated on clay balls

The product of formula (III) obtained in stage a) of Example 3 is used in the following way.

15 g of the product of formula (III) thus
10 prepared are slowly dusted over 100 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
15 of the glucose solution is sprayed. The product of formula (III) 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
20 6 h.

The catalyst (B₂) thus obtained, in accordance with the invention, consists of 4.3 % by weight of VSb_{3.5}Ga₂Ox/Al₂O₃ (25/75% by weight) coated on clay balls.

EXAMPLE 5 - Preparation of the catalyst (C)
according to the invention, of the
following empirical formula (IV):
 $\text{VSb}_{3.5}\text{In}_2\text{Ox}/\text{Al}_2\text{O}_3$ (25/75 % by weight)

5 **(IV)**

- a) A solution a) of ammonium vanadate is prepared by dissolving 1.5 g of NH_4VO_3 in 250 cm³ of demineralised water, a suspension (b) of antimony chloride is prepared by dissolving 6.53 g of Sb_2O_3 in 13.4 cm³ of 37 % hydrochloric acid and 150 cm³ of demineralised water, and a solution c) of indium nitrate is prepared by dissolving 10 g of $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 50 cm³ of demineralised water. Solution c), then suspension b) and then 30.3 g of Al_2O_3 are added to solution a) with stirring at approximately 80°C. The mixture is held at this temperature for 6 h and then 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 (IV) 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 then crushed to fragments with a particle size of between 0.3 and 0.8 cm constituting the catalyst C in accordance with the invention.

EXAMPLE 6 - Preparation of the catalyst (D)
according to the invention, of the
following empirical formula (V):

$\text{VSb}_5\text{Fe}_2\text{Ox}/\text{Al}_2\text{O}_3$ (25/75 % by weight)

- 5 a) A solution a) of ammonium vanadate is prepared by dissolving 2.34 g of NH_4VO_3 in 400 cm³ of demineralised water, a solution (b) of iron nitrate is prepared by dissolving 16.2 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 70 cm³ of demineralised water and
- 10 a suspension c) of antimony chloride is prepared by dissolving 14.6 g of Sb_2O_3 in 30 cm³ of 37 % hydrochloric acid and 300 cm³ of demineralised water. Solution b) is added to solution a) with stirring at approximately 70°C, and then
- 15 suspension c) is added. The mixture is brought to reflux and 47.3 g of Al_2O_3 are added. The mixture is held at this temperature for 6 h and evaporated to dryness, and the residue is dried at 120°C for approximately 15 h and then calcined at 550°C for
- 20 10 h.
- b) The product of formula (V) 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
- 25 pellets are then crushed to fragments with a particle size of between 0.3 and 0.8 cm constituting the catalyst D in accordance with the invention.

COMPARATIVE TEST 1 - Preparation of the catalyst
(E) not in accordance with the
invention, of the following
empirical formula:
 5 $\text{VSb}_{3.5}\text{Fe}_{0.1}\text{Ox}/\text{Al}_2\text{O}_3$ (25/75 % by
weight)

A product of composition $\text{VSb}_{3.5}\text{Fe}_{0.1}\text{Ox}/\text{Al}_2\text{O}_3$
 (25/75 % by weight) is prepared according to the
 following procedure. A solution (a) of ammonium
 10 vanadate is prepared by dissolving 2.34 g of NH_4VO_3 in
 400 cm³ of demineralised water, a solution b) of iron
 nitrate is prepared by dissolving 0.81 g of
 $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 70 cm³ of demineralised water and a
 suspension (c) of antimony chloride is prepared by
 15 dissolving 10.2 g of Sb_2O_3 in 21 cm³ of 37 %
 hydrochloric acid and 250 demineralised cm³. Solution
 (b) is added to solution (a) with stirring at
 approximately 70°C and then suspension (c) is added.
 The mixture is brought to reflux and 47.3 g of Al_2O_3 are
 20 added. 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
 25 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 $\text{VSb}_{3.5}\text{Fe}_{0.1}\text{Ox}/\text{Al}_2\text{O}_3$ (25/75 % by weight), not in accordance with the invention.

COMPARATIVE TEST 2 - Preparation of the catalyst

5 (F) 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)

10 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
15 antimony chloride is prepared by dissolving 10.2 g of
 Sb_2O_3 in 21 cm^3 of 37% hydrochloric acid and 230 cm^3
of demineralised water. Suspension (b), and then 47.3 g
of Al_2O_3 , are added to suspension (a) with stirring at
approximately 80-90°C. The mixture is maintained at
20 this temperature 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.

This product is then compressed under a
pressure of 4300 kg/cm^2 . Pellets are thus obtained with
25 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 (F), of composition

$\text{VSb}_{3.5}\text{Ox}/\text{Al}_2\text{O}_3$ (25/75 % by weight), not in accordance with the invention.

GENERAL PROCEDURE FOR THE AMMOXIDATION TESTS

The catalyst sample is brought beforehand to
 5 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.

10 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
 15 $36,000 \text{ h}^{-1}$, whose precise value will be shown for each
 Example.

Catalyst volume:

(catalytic phase + possible support): 25 cm^3 .

When the volume of the catalyst used will be
 20 different from this value, the specific value will be
 shown in the Examples.

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

- The catalyst is brought to a temperature
 25 T_1 , for example 300°C , and, after
 stabilising 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 moles) =
converted propane/introduced propane
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 conversion percentages and the selectivities are determined every 40 min.

In the Examples below, the following conventions are used:

20	DC(C ₃ H ₈)	=	conversion of propane
	S(ACN)	=	selectivity for acrylonitrile
	S(ACN+C ₃ H ₆)	=	selectivity for acrylonitrile and propylene
25	S(COx)	=	selectivity for carbon monoxide and carbon dioxide

5

EXAMPLE 7 AND COMPARATIVE TEST 3

catalysts (A₁) and (E).

10

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

15

$$\text{C}_3\text{H}_8 = 48 \%$$
$$\text{NH}_3 = 9 \%$$
$$O_2 = 18 \%$$
$$\text{H}_2\text{O} = 20 \%$$

20

He = 5 %

obtained are collated in Table 1 below.

Tests	Example 7				Comparative test 3			
Catalyst used	A ₁				E			
Temperature (in °C)	380	400	420	440	380	400	410	430
DC(C ₃ H ₈) %	9.5	12	11	10	7	12	13	19
S(ACN) %	34	36	38	33	2	10	9	17
S(ACN + C ₃ H ₈) %	60	63	71	76	49	42	41	41
S(Ammox) %	39	36	26	19	22	44	44	54
S(C ₁ C ₂) %	0	0	0	1	0	0	0	0
S(COx) %	0	0	2	4	29	14	15	5

TABLE 1

EXAMPLE 8 AND COMPARATIVE TEST 4

Measurement of the performances 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:

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 2 below.

Tests	Example 8					Comparative test 3				
Catalyst used	A ₁					E				
Temperature (in °C)	380	400	420	440	460	380	400	420	440	460
DC(C ₂ H ₆) %	2	5	15	31	38	4	8	15	26	42
S(ACN) %	18	34	66	74	66	9	18	31	27	34
S(ACN + C ₂ H ₆) %	79	65	78	81	75	44	44	50	39	43
S(Ammox) %	17	33	18	18	10	56	50	41	38	40
S(C ₁ C ₂) %	0	0	4	0	0	0	0	0	0	0
S(COx) %	4	2	0	0	15	0	7	10	22	17

TABLE 2

EXAMPLES 9 AND 10

Measurement of the performance of the catalyst(B₂).

The operating conditions used are the following:

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

The composition by volume of the reaction mixture, the temperature conditions (T(°C)) and the results obtained are collated in Table 3 below.

Examples	C_3H_6 (%)	NH_3 (%)	O_2 (%)	H_2O (%)	He (%)	T (°C)	DC (C_3H_8) (%)	S (ACN) (%)	S (ACN) + C_3H_6 (%)	S (Ammo x) (%)	S (C_1C_2) (%)	S (COx) (%)
Example 9	7.5	15	15	20	42.5	500	12.5	10	61	28	9	1
Example 10	25	10	25	20	20	480	6	10	68	27	4	0

TABLE 3

EXAMPLE 11

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:

10	C_3H_8	= 48 %
	NH_3	= 9 %
	O_2	= 18 %
	H_2O	= 20 %
	He	= 5 %

15 The temperature conditions and the results obtained are collated in Table 4 below.

		440°C	460°C	480°C
20	DC(C_3H_8) %	2	5	8.5
	S(ACN) %	15	38	46
	S(ACN + C_3H_6) %	86	86	82
	S(Ammox) %	6	11	15
	S(C_1C_2) %	8	3	3
	S(COx) %	0	0	0

TABLE 4

EXAMPLES 12 AND 13

Measurement of the performances of the catalysts (B₁) and (C).

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 %

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

Examples	Example 12				Example 13			
Catalyst used	B ₁				C			
Temperature (in °C)	400	420	440	460	400	420	440	460
20 DC(C ₃ H ₈) %	14	29	43	49	5	11	23	32
S(ACN) %	21	36	48	56	12	31	56	56
S(ACN + C ₃ H ₈) %	39	46	57	66	61	57	71	69
25 S(Ammox) %	58	43	37	26	39	37	25	17
S(C ₁ C ₂) %	0	0	0	0	0	0	4	1
S(COx) %	3	11	7	8	0	5	0	14

TABLE 5

EXAMPLE 14 AND COMPARATIVE TEST 5

Measurement of the performances of the catalysts (C) 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

5 mixture:

C₃H₈ = 40 %

NH₃ = 15 %

O₂ = 15 %

H₂O = 20 %

10 He = 10 %

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

Tests	Example 14				Comparative test 5			
	C				F			
Catalyst used								
Temperature (in °C)	400	420	440	460	400	420	440	460
DC(C ₃ H ₈) %	7	11	11	12	15	15	15	17
S(ACN) %	33	35	39	36	28	21	16	14
S(ACN + C ₃ H ₈) %	73	68	71	70	68	64	63	162
S(Ammox) %	21	23	20	19	26	28	26	23
S(C ₁ C ₂) %	0.	1	2	4	0.5	0	1	5
S(COx) %	5	8	7	7	6	8	11	10
	4							

TABLE 6

EXAMPLE 15

Measurement of the performance of the catalyst

25 (C) .

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:

30 C₃H₈ = 25 %

NH₃ = 25 %

O_2 = 10 %
 H_2O = 20 %
 He = 20 %

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

Temperature	400°C	420°C	440°C	460°C	480°C
DC (C_3H_8) %	7	13	13	13	13
S (ACN) %	34	32	37	42	46
S (ACN + C_3H_6) %	70	59	63	68	74
10 S (Ammox) %	30	40	30	26	19
S (C_1C_2) %	0	0	7	6	7
S (CO_x) %	0	0	0	0	0

TABLE 7

EXAMPLE 16

15 Measurement of the performance of the catalyst
 (A_1).

The operating conditions used are the following:

- Hourly volume rate = $1000\ h^{-1}$
- Total pressure = 1.3 bar
- 20 - Volume of the catalyst: $19\ cm^3$
- Composition by volume of the reaction
mixture:

25 C_3H_8 = 25 %
 NH_3 = 25 %
 O_2 = 10 %
 H_2O = 20 %
 He = 20 %

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

Temperature	380°C	400°C	420°C	440°C	460°C
DC (C ₃ H ₈) %	3	7	10	10	11
S (ACN) %	30	51	52	45	44
S (ACN + C ₃ H ₆) %	78	82	85	85	85
5 S (Ammox) %	23	19	15	15	15
S (C ₁ C ₂) %	0	0	0	0	0
S (COx) %	0	0	0	0	0

TABLE 8**EXAMPLE 17**

10 Measurement of the performance of the catalyst
(D).

The operating conditions used are the following:

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

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

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

Temperature (in °C)	360	380	400	420	440	460
DC(C ₃ H ₈) %	3	9	12	23	34	45
S(ACN) %	16	41	60	72	76	76
S(ACN + C ₃ H ₆) %	32	48	68	77	79	80
S(Ammox) %	68	53	31	19	13	12
S(C ₁ C ₂) %	0	0	0	0	0	0
S(COx) %	0	0	1	5	8	8

TABLE 9**EXAMPLE 18**

Measurement of the performance of the catalyst
(D).

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 = 20 %

NH₃ = 20 %

O₂ = 20 %

H₂O = 20 %

He = 20 %

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

Temperature	370°C	380°C	390°C	400°C
DC(C ₃ H ₈) %	2	4	7	11
S(ACN) %	18	28	43	56
S(ACN + C ₃ H ₆) %	42	49	58	68
S(Ammox) %	58	51	42	32
S(C ₁ C ₂) %	0	0	0	0
S(COx) %	0	0	0	1

TABLE 10

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,
- M represents an iron and/or gallium and/or
indium atom,
- b represents a whole or fractional number
equal to or greater than 0.5,
- 15 - 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
20 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
25 number up to 20 and is preferably between 1
and 10.

3. Process according to one of Claims 1 or
2, characterised in that the alkane is propane.



4. Process according to one of Claims 1 to 3, characterised in that the reaction is carried out in the presence of steam.

5 4, characterised in that the reaction temperature is between 300°C and 550°C and preferably between 350°C and 500°C.

6. Process according to one of Claims 1 to 5, characterised in that the total pressure is between 10 1 and 6 bar.

7. Process according to one of Claims 1 to 6, characterised in that the hourly volume rate is between 100 and 36,000 h⁻¹.

8. Process according to one of Claims 1 to 15 7, 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 9. Process according to one of Claims 1 to 8, characterised in that the composition of the gaseous mixture is outside the explosive region.

10. Process according to one of Claims 1 to 9, characterised in that the solid catalyst contains, 25 besides the said active phase, at least one inorganic oxide.

11. Process according to Claim 10, characterised in that the inorganic oxide is chosen



from alumina, silica, silica/alumina, zirconia, cerite, magnesia, titanium oxide, niobium oxide and their mixtures.

12. Process according to one of Claims 1 to 5 9, characterised in that the solid catalyst contains, besides the said active phase, an inert support or a ceramic or metal substrate of monolithic type.

13. Process according to either of Claims 10 and 11, characterised in that the solid catalyst also 10 contains an inert support or a ceramic or metal substrate of monolithic type.

14. Process according to either of Claims 10 and 11, characterised in that the active phase of the catalyst represents from 5 % to 100 % by weight of the 15 weight of the said catalyst and preferably from 10 % to 50 % weight/weight.

15. Process according to either of Claims 12 and 13, characterised in that the active phase or the catalytic phase represents from 1 % to 50 % by weight 20 of the weight of the catalyst and preferably from 5 % to 35 % weight/weight.

ABSTRACT

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 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, iron and/or gallium and/or indium and oxygen.

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

