

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

5 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 hydrocarbons, which are more widely available, are more
10 advantageous starting materials from an economic viewpoint, it is also well known that they do not have a comparable reactivity in this type of reaction, in particular to form α,β -unsaturated nitriles.

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

 It has already been proposed, in US Patent No. 3,365,482, to ammoxidize, in particular 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 % with
5 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 % with a degree of conversion of
10 the propane of 29 %.

In French Patent 2,027,238 (corresponding in part to US Patent No. 3,670,009), a process is proposed for the vapour phase ammoxidation of saturated hydrocarbons at a temperature above 500°C over a solid
15 catalyst which can, in particular, consist of tin oxide, boron oxide, molybdenum oxide and silicon oxide. Thus, in Example IX of the table on pages 12-13, the selectivity for acrylonitrile reaches 35 %, at 32 % conversion of the propane, but with operating
20 conditions which place the propane/ammonia/air (1/1.2/12) reaction mixture in the explosive region.

In French Patent 2,072,334 (corresponding to British Patent No. 1,336,135), a process is recommended for the catalytic ammoxidation of alkanes, in the
25 vapour phase, at a temperature below 500°C, with a high concentration of alkane in the feed gas mixture, over a solid catalyst which can, in particular, consist of tin oxide and of molybdenum oxide (90/10 by weight);

however, better performances are obtained with catalysts consisting of antimony oxide and of vanadium oxide.

In French Patent 2,072,399, a process is also
5 proposed for the catalytic ammoxidation of alkane, in the vapour phase, with a high concentration of alkane in the feed gas mixture, over a solid catalyst which can, in particular, be a binary mixture of oxides containing molybdenum oxide.

10 The following pairs are more particularly indicated:

(Mo, Sb) (Mo, Sn) (Mo, V) (Mo, Ti) (Mo, Bi).

However, none of these pairs has a better
performance than those obtained with pairs not
15 containing molybdenum. The acrylonitrile yields obtained are very low; at best, 1.7 % of the propane is converted to acrylonitrile at 570°C over a catalyst based on oxides of tin and of titanium.

In French Patent No. 2,119,492 (corresponding
20 to US Patent No. 3,746,737 and to British Patent No. 1,337,759), it is proposed to use a binary composition based on oxides of molybdenum and of cerium. However, the performance of the (Mo, Ce) pair appears inadequate in the absence of halogen or of a halogenated compound.

25 It is additionally recommended to add, to this (Mo, Ce) binary composition, a third element chosen from tellurium and bismuth (cf. also US 3,833,638). There again, the performance of the

catalytic system appears inadequate in the absence of halogen or of a halogenated compound. In addition, it will be noted that, in the presence of CH_3Br , the selectivity for acrylonitrile reaches 67 %, at 98 % conversion of the propane, but under operating conditions which place the propane/ammonia/air (1/1.2/12) reaction mixture in the explosive region.

French Patent No. 2,119,493 has also provided for the ammoxidation of alkanes in the vapour phase over a solid catalyst containing oxides of bismuth and of molybdenum and, if appropriate, of phosphorus and of silica.

There again, the performance of the catalytic system appears inadequate in the absence of halogen or of a halogenated compound and the reaction mixture is within the explosive region.

In the face of these many shortcomings, various work, in parallel or subsequently, has focused on the use of solid catalysts based on vanadium and/or on antimony.

In "Chemistry Letters, 1989 (pp. 2173-2176)", the writers tested, in the ammoxidation of propane in the vapour phase, multicomponent metal oxides containing molybdenum and bismuth and having a structure of the scheelite type. It appears that, despite the relatively moderate temperatures used, the proportion of combustion products (CO , CO_2) is very high in all cases (at least 15 %) and that some

catalytic compositions tested have very little activity with respect to the desired reaction, despite their use under conditions which lie in the explosive region or very near the said region.

5 The presence of a halogenated compound is capable of inducing corrosion of the equipment and is therefore undesirable in an industrial process.

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

 In addition, the use of reaction mixtures which lie in the explosive region is even less desirable on an industrial scale since the process is used in a stationary bed.

15 It therefore appears that it would be highly 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
20 nitrile, in particular acrylonitrile, while reducing, as much as it is possible to do so, the losses in starting material as a result of the formation of oxides of carbon.

25 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 subject of the present invention is therefore a process for the ammoxidation of alkanes in the vapour phase in the presence of a solid catalyst, the active phase of which contains molybdenum, vanadium and oxygen, characterized in that the said active phase also contains at least one element chosen from manganese, zinc, cobalt, copper, lithium, sodium, potassium and silver.

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 steam content 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.

The content of saturated hydrocarbon in the reactive gas is preferably between 5 and 70 %. That of ammonia is preferably between 3 and 45 % 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 reactive mixture will be outside the explosive region. For the ammoxidation of propane in the absence of inert diluent, the composition (propane, oxygen, ammonia) will be advantageously chosen from within the quadrilateral ABDE which appears in the ternary diagram ABC represented in the single appended Figure.

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 within segment BC, corresponds to a propane content of 45 %; in the binary system (propane/O₂); point E, situated within segment AC, corresponds to an ammonia content of 79 % in the binary system (NH₃)/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.

For 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 a low proportion.

For 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 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 within segment BC, corresponds to a propane content of 16 % in the binary system (propane/air); point G, situated within 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 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

oxygen content equivalent to that of air ($\approx 21\%$ oxygen) or in the case where this mixture is deficient in oxygen with respect to air.

Starting from propane, a mixture will be
5 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
10 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
15 more particularly suitable for the ammoxidation of propane.

While the saturated hydrocarbon used may be of technical grade, it will not contain significant quantities of compounds containing ethylenic
20 unsaturation. Thus, the propane employed will only contain trace quantities of propylene.

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

The reaction temperature is generally between 350 and 550°C and, preferably, between 410 and 510°C.

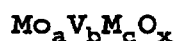
The total pressure of the reaction mixture can be greater than or equal to atmospheric pressure.

5 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.

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 present invention, use is made of a solid catalyst in which the active phase corresponds to the empirical formula



in which:

20 - M represents one or a number of elements chosen from manganese, zinc, cobalt, copper, lithium, sodium, potassium and silver.

- a is a non-zero number less than 2;

- b is a non-zero number less than 2;

25 - c is a non-zero number less than 1; and

- x is determined by the oxidation number of the other elements.

M preferably represents one or a number of

elements of which at least one is chosen from manganese, zinc and cobalt.

Preferably, in the empirical formula involved,

- 5 - a is between 0.1 and 1 inclusive;
 - b is between 0.05 and 1.8 inclusive; and
 - c is between 0.1 and 1 inclusive.

Active phases which are more particularly preferred correspond to the empirical formula involved and in which:

10

- M represents an element chosen from manganese, zinc and cobalt
 - a is between 0.1 and 1 inclusive;
 - b is between 0.05 and 1.8 inclusive;
15 - c is between 0.1 and 1 inclusive; and

The active phases involved can be used, in the context of the process according to the invention, in the bulk form or in the particulate state. These phases can be used in the form of powders or of balls, which are extruded or crushed, for example.

20

They can also be deposited on an inert support or can coat it. The nature of the 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,

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silica/alumina, sintered clay, carborandum, magnesia, magnesium silicate and diatomaceous earth. This support is preferably nonporous and can especially be based on a refractory oxide in the particulate form, the most
5 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 by those skilled in the art as
10 a function of the acceptable pressure drop in the reactor. The 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
15 inert and rigid structure of monolithic type comprising channels or ducts. Such supports are well known to those skilled in the art and have been widely described in the literature. The substrates used which are made of ceramic substance are especially those containing,
20 as the main substance, cordierite, alumina, mullite, porcelain, and carbides of boron or of silicon.

When a coated catalyst is used, the quantity of active phase, which can vary within wide limits, is in practice between 5 and 35 % and preferably between 8
25 and 20 % by weight with respect to the combination (support + active phase).

The preparation of the catalysts used in the process according to the invention can be carried out

in various ways known per se, such as mixing of suitable salts of the constituent elements in water or in 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.

The most commonly employed suitable salts are soluble in water and contain anions or cations which can be decomposed by heat during the subsequent stages. These are, for example, ammonium heptamolybdate for molybdenum, ammonium vanadate for vanadium, and manganese, zinc and cobalt nitrates or chlorides.

Once the mixture of the salts has been prepared, a precursor can be obtained by the so-called evaporation method. The water of the suspension obtained is evaporated by heating between 20 and 100°C with stirring for the time necessary for a non-runny paste to be obtained. Stirring and heating are then halted.

The paste thus obtained, spread in a thickness of approximately 2 cm, is dried under air at approximately 120°C for approximately 15 h. The precursor thus obtained can then be ground and calcined between 200 and 1,000°C, preferably between 400 and 600°C, for at least 30 min and preferably at least one hour: it may prove to be useful to carry out a number of grinding and calcining operations in succession.

Calcination can be carried out by progressively raising the temperature, for example 100 to 200°C per hour, due, in particular, to the risks related to the exothermic decomposition of ammonium nitrate at approximately 230°C. The active 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 variation comprising precipitation with addition, for example, of aqueous ammonia or of hydrochloric acid at the end of mixing of the salts, in order to stabilize the pH at approximately 7. It is preferable to heat the suspension between 20 and 100°C for approximately 1 hour to bring precipitation of the species to completion.

The suspension is then filtered and washed. The filter cake is then spread out and then dried, ground and calcined according to the conditions described above in the context of the evaporation method, to give the active phase. A number of active phases can be mixed to give a new active phase, for example in a mortar.

Some catalysts, useful for an implementation of the process in a stationary bed, can be obtained by coating ground, intermediate or finished, active phases in a manner known per se. This conventional method consists in depositing a layer of intermediate or finished active phase around inert but rough balls.

Once the balls are covered with the desired quantity of the active phase, they are dried with hot air between 70 and 150°C for at least 30 minutes and then are introduced into an oven in order to be
5 calcined between 300 and 600°C, preferably between 450 and 500°C, for at least 3 hours.

Some catalysts which are useful for an implementation of the process according to the invention in a moving bed or fluidized 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 between 5 and 100 μm in size are preferred in the context of use in a fluidized bed.

The products of the reaction can be recovered
20 from the effluent gases by any suitable means. For example, the effluent gases can pass into a condenser containing dilute sulphuric acid in order to neutralize the unconverted ammonia. The gases can then pass through a refrigerated absorbing column to condense the
25 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 a catalyst (A), the active phase of which corresponds to the formula $Mn_{0.8}V_{1.6}Mo_{0.4}O_6$

10 An active phase with the composition $Mn_{0.8}V_{1.6}Mo_{0.4}O_6$ is prepared according to the following procedure: a solution (a) of manganese nitrate is prepared by dissolving 204.91 g of 98 % $Mn(NO_3)_2 \cdot 4H_2O$ (marketed by the Company Prolabo) in 300 cm³ of
15 demineralized water, a solution (b) of ammonium heptamolybdate is prepared by dissolving 70.64 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (marketed by the Company Merck) in 200 cm³ of demineralized water and a suspension is prepared of 187.17 g of NH_4VO_3 (marketed by the company
20 Prolabo) in 400 cm³ of demineralized water. The solution (a) is poured into the suspension (c) in a stirred reactor. The solution (b) is then introduced, whilst still stirring. Vigorous stirring is carried out and the temperature is progressively raised to 100-
25 110°C. The paste obtained is dried at 120°C for approximately 15 h. The product obtained is then ground, calcined at 600°C for 6 h, reground and

recalcined at 600°C for 42 h.

The product (I) thus obtained has a specific surface, measured according to the B.E.T. method, of to $0.1 \text{ m}^2\text{g}^{-1}$.

5 20 g of the product (I) are slowly dusted over 123 g of inert support composed of clay balls with a mean diameter of 4.8 mm, placed beforehand in a rotary coating pan and moistened with 10% aqueous glucose solution. As soon as the balls are dry on the
10 outside, a small quantity of the glucose solution is sprayed. The product (I) is then again dusted onto the balls. These operations are continued alternately until all the product (I) has been coated on. Drying is then carried out at 120°C for 2 h and calcining at 480°C for
15 6 h.

The catalyst (A) thus obtained, in accordance with the invention, consists of 11.6 % by weight of $\text{Mn}_{0.8}\text{V}_{1.6}\text{Mo}_{0.4}\text{O}_6$ deposited on clay balls.

EXAMPLE 2: - Preparation of a catalyst (B), the
20 active phase of which corresponds to the formula $\text{Mn}_{0.8}\text{V}_{1.6}\text{Mo}_{0.4}\text{O}_6$

An active phase with the composition $\text{Mn}_{0.8}\text{V}_{1.6}\text{Mo}_{0.4}\text{O}_6$ is prepared according to the same procedure as in Example 1, except for the final
25 calcinations which are carried out in the following way: the product is ground, calcined at 450°C for 8 h, reground, recalcined at 450°C for 8 h, reground,

calcined at 550°C for 4 h, and reground and recalcined at 550°C for 4 h.

The product (I) thus obtained and has a specific surface, measured according to the B.E.T.

5 method, of $1.7 \text{ m}^2\text{g}^{-1}$.

20 g of the product (I) are slowly dusted over 123 g of inert support composed of clay balls with a mean diameter of 4.8 mm, placed beforehand in a rotary coating pan and moistened with 10% aqueous
10 glucose solution. As soon as the balls are dry on the outside, a small quantity of the glucose solution is sprayed. The product (I) is then again dusted onto the balls. These operations are continued alternately until all the product (I) has been coated on. Drying is then
15 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 10 % by weight of $\text{Mn}_{0.8}\text{V}_{1.6}\text{Mo}_{0.4}\text{O}_6$ deposited on clay balls.

20 EXAMPLE 3: - Preparation of a catalyst (C), the active phase of which corresponds to the formula $\text{Zn}_{0.85}\text{V}_{1.7}\text{Mo}_{0.3}\text{O}_6$

An active phase with the composition $\text{Zn}_{0.85}\text{V}_{1.7}\text{Mo}_{0.3}\text{O}_6$ is prepared according to the following
25 procedure: a solution (a) of zinc nitrate is prepared by dissolving 252.8 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (marketed by the Company Prolabo) in 250 cm^3 of demineralized water, a

solution (b) of ammonium heptamolybdate is prepared by dissolving 52.95 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (marketed by the Company Merck) in 150 cm³ of demineralized water and a suspension is prepared of 165.75 g of NH_4VO_3 (marketed by the Company Prolabo) in 210 cm³ of demineralized water. The two solutions (a) and (b) are mixed and this mixture is poured into the suspension (c) in a stirred reactor. The mixture is left stirring for 20 h and the temperature is progressively raised to 100-110°C. The mixture is left at reflux for 1 h and evaporated. The paste obtained is dried at 120°C for approximately 15 h. The product obtained is then ground, calcined at 250°C for 4 h, reground and calcined at 450°C for 8 h, reground and recalcined at 450°C for 8 h, reground and calcined at 550°C for 4 h, and reground and recalcined at 550° for 4 h.

The product (I) thus obtained has a specific surface, measured according to the B.E.T. method, of 0.8 m²g⁻¹.

20 g of the product (I) are slowly dusted over 123 g of inert support composed of clay balls with a mean diameter of 4.8 mm, placed beforehand in a rotary coating pan 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 (I) is then again dusted onto the balls. These operations are continued alternately until all the product (I) 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, in accordance with the invention, consists of 12 % by weight of

5 $\text{Zn}_{0.85}\text{V}_{1.7}\text{Mo}_{0.3}\text{O}_6$ deposited on clay balls.

EXAMPLE 4: - Preparation of a catalyst (D), the active phase of which corresponds to the formula $\text{Co}_{0.9}\text{V}_{1.8}\text{Mo}_{0.2}\text{O}_6$

An active phase with the composition

10 $\text{Co}_{0.9}\text{V}_{1.8}\text{Mo}_{0.2}\text{O}_6$ is prepared in the following way: 84 g of NH_4VO_3 are suspended in 100 cm³ of demineralized water, a solution of ammonium heptamolybdate is prepared by dissolving 14 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ in 100 cm³ of demineralized water and a solution of cobalt
15 nitrate is prepared by dissolving 105 g of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ in 100 cm³ of demineralized water. The solution of ammonium heptamolybdate is run onto the suspension of ammonium metavanadate in a stirred reactor. The
20 solution of cobalt nitrate is then introduced, whilst still stirring. After stirring for 20 h at room temperature, evaporation is carried out to dryness and the residue is dried at 120°C and then calcined at 250°C for 4 h. The product obtained is ground and is
25 subjected to the following calcinations-grindings cycle:

450°C for 4 h - grinding

450°C for 4 h - grinding

450°C for 8 h - grinding

550°C for 4 h - grinding

550°C for 4 h - grinding

The product (I) thus prepared has a specific
5 surface, measured according to the B.E.T. method, of
2 m²g⁻¹.

15 g of the product (I) 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
10 rotary coating pan 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 (I) is then again dusted onto the
balls. These operations are continued alternately until
15 all the product (I) 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 (D) thus obtained, in accordance
with the invention, consists of 12 % by weight of
20 Co_{0.9}V_{1.8}Mo_{0.2}O₆ deposited on clay balls.

EXAMPLE 5: - Preparation of a catalyst (E), the
active phase of which corresponds to the
formula Mn_{0.8}V_{1.6}Mo_{0.4}O₆

The product (I), with the composition
25 Mn_{0.8}V_{1.6}Mo_{0.8}O₆ is prepared according to the following
procedure: a solution (a) of manganese nitrate is
prepared by dissolving 153.7 g of Mn(NO₃)₂·4H₂O in

225 cm³ of demineralized water, a solution (b) of ammonium heptamolybdate is prepared by dissolving 141.28 g of (NH₄)₆Mo₇O₂₄·4H₂O in 400 cm³ of demineralized water and a suspension (c) is prepared of 140 g of
5 NH₄VO₃ in 150 cm³ of demineralized water. The mixture of the solutions (a) and (b) is poured into the suspension (c) in a stirred reactor. Stirring is carried out for approximately twenty hours and the temperature is progressively raised to 100-110°C. The paste obtained
10 is dried at 120°C for approximately 15 h. The product is calcined under air at 250°C for 4 h, ground, calcined at 450°C for 8 h, reground, recalcined at 450°C for 8 h, reground, calcined at 550°C for 4 h, and reground and recalcined at 550°C for 4 h.

15 A product (II), with the composition αMnV₂O₆, is then prepared according to the procedure described by R. Kozlowski, J. Ziolkowski, K. Mocala & J. Haber, J. Sol. State Chem., 35, 1-9 (1980): a solution of manganese nitrate is prepared by dissolving 256.13 g of
20 Mn(NO₃)₂·4H₂O in 300 cm³ of demineralized water. 116.98 g of NH₄VO₃ are suspended in 200 cm³ of demineralized water. The solution of manganese nitrate is poured into the suspension of ammonium metavanadate in a stirred reactor. After stirring for 10 to 15 min
25 at room temperature, filtration is carried out on sintered glass and washing is carried out with 2 litres of demineralized water. The product obtained is then dried at 120°C for approximately 15 h and then calcined

under air for 5 h at 500°C.

15 g of product (I) and 15 g of the product (II) which are thus obtained are mixed in a mortar.

The product (III) thus prepared, with the
5 overall composition $\text{Mn}_{0.8}\text{V}_{1.6}\text{Mo}_{0.4}\text{O}_6$, has a specific surface, measured according to the B.E.T. method, of $3 \text{ m}^2\text{g}^{-1}$.

10 10 g of the product (III) are slowly dusted over 67 g of inert support composed of clays balls with a mean diameter of 4.8 mm, placed beforehand in a rotary coating pan 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. A small quantity of the glucose solution is
15 then dusted. The product (III) is then again dusted onto the balls. These operations are continued alternately until all the product (III) has been coated on. Drying is then carried out at 120°C for 2 h and calcined at 480°C for 6 h.

20 The catalyst (E) thus obtained, in accordance with the invention, consists of 12.4 % by weight of $\text{Mn}_{0.8}\text{V}_{1.6}\text{Mo}_{0.4}\text{O}_6$ deposited on clay balls.

EXAMPLE 6

- Preparation of a catalyst (F), the
active phase of which corresponds to the
25 formula $\text{Mn}_{0.4}\text{V}_{0.05}\text{Mo}_{0.4}\text{O}_{1.75}$

A product (I) with the composition
 $\text{Mn}_{0.4}\text{V}_{0.05}\text{Mo}_{0.4}\text{O}_{1.75}$ is prepared according to the

following procedure: a solution (a) of manganese chloride is prepared by dissolving 79.16 g of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in 300 cm^3 of demineralized water and a solution (b) of ammonium heptamolybdate is prepared by dissolving 70.6 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in 300 cm^3 of demineralized water. 4.52 g of V_2O_5 and then the solution (b) are added to the solution (a) in a stirred reactor. 40 cm^3 of NH_4OH (20 % NH_3) are then added and heating is carried out at reflux for 3 h. Filtration is carried out on sintered glass and washing is carried out with 1 l of demineralized water. The product obtained is then dried at 120°C for approximately 15 h and then calcined under air at 500°C for 4 h.

10 g of the product (I) thus obtained are slowly dusted over 67 g of inert support composed of clay balls with a mean diameter of 4.8 mm, placed beforehand in a rotary coating pan 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 (I) is then again dusted onto the balls. These operations are continued alternately until all the product (I) 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 (F) thus obtained, in accordance with the invention, consists of 9.1 % by weight of $\text{Mn}_{0.4}\text{V}_{0.05}\text{Mo}_{0.4}\text{O}_{1.75}$ deposited on clay balls.

Control test (a): Preparation of a catalyst (a) which does not come within the scope of the invention and in which the active phase corresponds to the formula MnV_2O_6 .

The product (II) prepared in Example 5 above has a specific surface, measured according to the B.E.T. method, of $5 \text{ m}^2\text{g}^{-1}$. This product is known as product (I) in the present example.

20 g of the product (I) are slowly dusted over 123 g of inert support composed of clay balls with a mean diameter of 4.8 mm, placed beforehand in a rotary coating pan 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 (I) is then again dusted onto the balls. These operations are continued alternately until all the product (I) 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 (a) thus obtained, not in accordance with the invention, consists of 13 % by weight of $\alpha\text{MnV}_2\text{O}_6$ deposited on clay balls.

Control test (b): Preparation of a catalyst (b) which does not come within the scope of the invention and in which the active phase corresponds to the

formula ZnV_2O_6 .

A solution of zinc nitrate is prepared by dissolving 148.7 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (marketed by the Company Prolabo) in 200 m³ of demineralized water.

5 117 g of NH_4VO_3 (marketed by the company Prolabo) are suspended in 200 cm³ of demineralized water. The solution of zinc nitrate is poured into the suspension of ammonium metavanadate in a stirred reactor. After stirring for 23 h at room temperature, filtration is
10 carried out on sintered glass and washing is carried out with 400 cm³ of demineralized water. The product obtained is then dried at 120°C for approximately 15 h and then calcined under air for 5 h at 500°C.

The product (I) thus obtained has a specific
15 surface, measured according to the B.E.T. method, of 3 m²g⁻¹.

20 g of the product (I) are slowly dusted over 123 g of inert support composed of clay balls with a mean diameter of 4.8 mm, placed beforehand in a
20 rotary coating pan 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 (I) is then again dusted onto the balls. These operations are continued alternately until
25 all the product (I) 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, not in

accordance with the invention, consists of 16 % by weight of ZnV_2O_6 deposited on clay balls.

Control test (c): Preparation of a catalyst (c) which does not come within the scope of the invention and in which the active phase corresponds to the formula CoV_2O_6

An active phase with the composition CoV_2O_6 is prepared in the following way: 117 g of NH_4VO_3 are suspended in 200 cm^3 of demineralized water and a solution of cobalt nitrate is prepared by dissolving 145.5 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 200 cm^3 of demineralized water. The solution of cobalt nitrate is run onto the suspension of ammonium metavanadate in a stirred reactor. After stirring for 23 h at room temperature, filtration is carried out on sintered glass and washing is carried out with 3 times 200 cm^3 of demineralized water. The product obtained is then dried at 120°C for approximately 15 h and then calcined under air for 5 h at 500°C.

The product (I) thus prepared has a specific surface, measured according to the B.E.T. method, of 3.6 m^2g^{-1} .

15 g of the product (I) 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 pan 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 (I) is then again dusted onto the balls. These operations are continued alternately until
5 all the product (I) 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 12 % by
10 weight of CoV_2O_6 deposited on clay balls.

GENERAL PROCEDURE FOR THE AMMOXIDATION TEST -

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
15 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 is 1.3 bar abs.

20 The gas flow rate is defined so as to have an hourly volume rate (HVR) of $1,000 \text{ h}^{-1}$, except when otherwise mentioned.

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

25 - The catalyst is brought to a temperature T_1 , for example 300°C, and, after stabilizing for 30 min at the temperature T_1 , the composition of the

mixture at the reactor outlet is determined by gas phase chromatography.

- The conversion percentages and the selectivities obtained on the catalyst examined at the inlet temperature T_1 are calculated using relationships of the type:

Conversion of propane = % converted propane/
% introduced propane

Selectivity for acrylonitrile = % propane converted to
acrylonitrile/% converted propane

- The catalyst is then brought from 300 to 550°C by increments of 20 to 30°C and the conversion percentages and the selectivities are determined every 40 min.

In the Examples below, the following conventions are used:

DCC3H8 = conversion of propane
SACN = selectivity for acrylonitrile
SACN+C3H6 = selectivity for acrylonitrile and propylene
SCOX = selectivity for carbon monoxide and carbon dioxide.

EXAMPLE 7: control test (d) -

The performances of the catalysts (A) and (a) at various temperatures and under the following shared conditions are determined:

- Catalyst volume (active phase + clay balls) = 20 cm³
- Total flow rate of the synthetic mixture = 20 l.h⁻¹
- Composition of the said mixture =

C₃H₈ = 19.0 % (% by volume)

NH₃ = 7.5 %

O₂ = 10.0 %

H₂O = 25.0 %

He = 38.5 %

The results and the specific conditions

appear in Table I below:

TABLE I

REF.	CATALYST	T°C	DCC3H8 (%)	SACN (5)	SACN+ C3H6 (%)	SCOX (5)
control d	(a)	420	11	12	34	22
		445	12	2.5	35	27
		470	15	0	37	31
Exam. 7	(A)	420	2	8	79	0
		470	11	25	63	2
		510	19	29	58	11

EXAMPLE 8: control test (e):

The performances of the catalysts (C) and (b) are determined at 480°C and under the following shared conditions:

- Catalyst volume (active phase + clay balls) = 25 cm³
- Total flow rate of the synthetic mixture = 25 l.h⁻¹
- Composition of the said mixture =

C_3H_8 = 20.0 % (% by volume)

NH_3 = 5.0 %

O_2 = 15.0 %

H_2O = 20.0 %

He = 40.0 %

5

The results and the specific conditions appear in Table II below:

TABLE II

REF.	CATALYST	DC3H8 (%)	SACN (%)	SACN+ C3H6 (%)	SCOX (%)
control e	(b)	14	0	44	39
Example 8	(C)	9	10	38	17

10

EXAMPLE 9: control test (f):

The performance of the catalysts (D) and (c) are determined at various temperatures and under the following shared conditions:

15

- Catalyst volume (active phase + clays balls) = 25 cm³
- Total flow rate of the synthetic mixture = 25 l.h⁻¹
- Composition of the said mixture =

C_3H_8 = 7.5 % (% by volume)

NH_3 = 15.0 %

O_2 = 15.0 %

H_2O = 20.0 %

He = 42.5 %

20

The results and the specific conditions appear in Table III below:

25

TABLE III

REF.	CATALYST	T°C	DCC3H8 (%)	SACN (%)	SACN+ C3H6 (%)	SCOX (%)
control f	(c)	415	4	1	89	1
		435	9	2	57	25
		455	19	0	26	31
5 Example 9	(D)	415	5	12	78	0
		435	8	8	72	9
		455	16	18	51	16

EXAMPLE 10 TO 21 -

The performances of various catalysts whose preparation is the objective of Examples 1 to 6 above are determined under various conditions at an hourly spatial rate (HVR) of 1,000 h⁻¹.

The reference of the catalyst used, the specific conditions employed and the results obtained appear in Table IV below:

TABLE IV

Reference	Example 10			Example 11			Example 12			Example 13			Example 14			Example 15			Example 16			Example 17		
CATALYST	(A)			(B)			(A)			(B)			(D)			(E)			(E)			(F)		
Composition(*)	% Volume			% Volume			% Volume			% Volume			% Volume			% Volume			% Volume			% Volume		
	11	19	26	20			19	20			40			48			40			15				
	7.5			5	15	25	7.5			15			9			15			15					
	10			15			4	10	16.5	5	15	25	18			20			20					
	25			20			25			20			20			20			20					
He	qsp 100 %			qsp 100 %			qsp 100 %			qsp 100 %			10			5			10					
T°C	470			460			470			460			440			430			450			480		
%	9	11	3	11	11	11	6	11	12	5	11	7	15	14	14	8	8	8	9	9	10	10		
	18	25	7	20	14	8	16	25	21	12	14	7	22	22	27	14	14	12	12	18	18			
	65	63	88	59	48	47	78	63	54	81	48	68	57	60	64	63	63	62	64	69	69			
	8	2	0	0	0	0	5	2	12	0	0	0	0	0.2	0	6	5	5	9	4	4			

(*) : of the gas mixture

Reference	Example 18	Example 19	Example 20	Example 21
CATALYST	(D)		(F)	
Composition (*)	% Volume	% Volume	% Volume	% Volume
C ₃ H ₈	25	25	25	7.5
NH ₃	10	25	10	15
O ₂	25	10	25	15
H ₂ O	20	20	20	20
He	20	20	20	42.5
T°C	420	440	440	480
%				
DDC ₃ H ₈	12	5	5	13
S AN	18	11	10	22
S AN+C ₃ H ₆	51	77	72	52
S COX	0	0	0	0

CLAIMS

1. Process for the ammoxidation of alkanes in the vapour phase in the presence of a solid catalyst, characterized in that the active phase of the said catalyst corresponds to the empirical formula $\text{Mo}_a\text{V}_b\text{M}_c\text{O}_x$ in which:

- M represents one or a number of elements chosen from manganese, zinc, cobalt, copper, lithium, sodium, potassium and silver.

- a is a non-zero number less than 2;
- b is a non-zero number less than 2;
- c is a non-zero number less than 1; and
- x is determined by the oxidation number of the other elements.

2. Process according to claim 1, characterized in that the said active phase corresponds to the said empirical formula in which M represents one or a number of elements of which at least one is chosen from manganese, zinc and cobalt.

3. Process according to claim 1 or 2, characterized in that the said active phase corresponds to the empirical formula in which:

- a is a number between 0.1 and 1 inclusive;
- b is a number between 0.05 and 1.8 inclusive; and
- c is a number between 0.1 and 1 inclusive.

4. Process according to any one of claims 1 to 3, characterized in that the said active phase corresponds to the empirical formula in which:



- M represents an element chosen from manganese, zinc and cobalt
- a is a number between 0.1 and 1 inclusive;
- b is a number between 0.05 and 1.8 inclusive; and
- c is a number between 0.1 and 1 inclusive.

5

5. Process according to any one of the preceding claims, characterized in that the alkane is propane.

10

6. Process according to any one of the preceding claims, characterized in that the reaction is carried out in the presence of steam.

7. Process according to any one of the preceding claims, characterized in that the reaction temperature is between 350°C and 550°C.

15

8. Process according to any one of the preceding claims, characterized in that the total pressure is between 1 and 6 Bar.

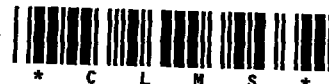
9. Process according to any one of the preceding claims, characterized in that the hourly volume rate is between 100 and 36,000 h⁻¹.

20

10. Process according to any one of the preceding claims, characterized 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 45 % and the content of oxygen is between 3 and 45 %.

25

11. Process according to any one of the preceding claims, characterized in that the composition of the



gaseous mixture is outside the explosive region.

12. Process according to any one of the preceding claims, characterized in that the solid catalyst contains, besides the said active phase, a support.