

PROCESS FOR AMMOXIDATION OF SATURATED HYDROCARBONS

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

It is well known to those skilled in the art that very many propositions have been formulated with regard to the ammoxidation of olefins and, in particular, that of propylene. However, although saturated hydrocarbons, which are more widely available, are raw materials which are of greater interest from the standpoint of economics, they are also well known not to exhibit a comparable reactivity in this type of reaction for forming α, β -unsaturated nitriles in particular.

One of the difficulties encountered in the ammoxidation of saturated hydrocarbons lies in the need to have access to catalysts capable of dehydrogenating the saturated hydrocarbon under conditions which minimise or suppress the combustion of ammonia and/or that of the hydrocarbon while ensuring a reasonable selectivity either for α, β -unsaturated nitrile (the target product), for example for acrylonitrile when starting with propane, or for products which can be turned to profit (abovementioned nitrile and olefin), for example for acrylonitrile and propylene when

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starting with propane.

In US Patent No. 3 365 482 it has already been proposed to ammoxidize isobutane in particular to methacrylonitrile on a catalyst based on molybdenum deposited on eta-alumina, doped with antimony at 508°C, starting with a gaseous mixture containing isobutane, air, ammonia and water vapour (1.0/4.5/1.0/12.5); the selectivity for methacrylonitrile reaches 49 % with an isobutane conversion of 22 %.

When starting with a gaseous mixture of propane/air/ammonia/water vapour (1.0/4.7/0.67/12.8) with the same catalyst and at 550°C, the selectivity for acrylonitrile drops to 15 % with a propane conversion of 29 %.

French Patent 2 027 238 (corresponding partially to US Patent No. 3 670 009) proposes a vapour phase process for ammoxidation of saturated hydrocarbons at a temperature above 500°C on a solid catalyst which may consist especially 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 %, with a 32 % propane conversion, but with operating conditions placing the propane/ammonia/air reaction mixture (1/1.2/12) in the explosive region.

French Patent 2 072 334 (corresponding to British Patent No. 1 336 135) recommends a vapour phase process for catalytic ammoxidation of alkanes at a

temperature below 500°C with a high concentration of alkane in the gaseous mixture fed, on a solid catalyst which may consist especially of tin oxide and molybdenum oxide (90/10 by weight); however, better
5 performance is obtained with catalysts consisting of antimony oxide and vanadium oxide.

French Patent 2 072 399 also proposes a process for catalytic ammoxidation of alkane, in vapour phase, with a high concentration of alkane in the
10 gaseous mixture fed, on a solid catalyst which may be especially a binary mixture of oxides including molybdenum oxide.

The following pairs should be mentioned in particular:

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

However none of these pairs offers a performance which is better than those obtained with pairs which do not contain molybdenum. The acrylonitrile yields obtained are very low; at best,
20 1.7 % of the propane is converted into acrylonitrile at 570°C on a catalyst based on tin and titanium oxides.

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

It is additionally recommended to add to this binary composition (Mo, Ce) a third element chosen from tellurium and bismuth (cf. also US 3 833 638). Here, too, the performance of the catalyst system appears to be insufficient in the absence of halogen or of a halogen compound. What is more, it will be noted that in the presence of CH_3Br the selectivity for acrylonitrile reaches 67 % with 98 % propane conversion, but under operating conditions which place the propane/ammonia/air reaction mixture (1/1, 2/12) in the explosive region.

In French Patent No. 2 119 493 it has also been proposed to carry out the vapour phase ammoxidation of alkanes on a solid catalyst containing bismuth and molybdenum oxides and, if appropriate, phosphorus and silica.

Here, too, the performance of the catalyst system appears to be insufficient in the absence of halogen or of a halogen compound and the reaction mixture is in the explosive region.

Confronting these numerous shortcomings, various parallel or subsequent investigations have been concerned with the use of solid catalysts based on vanadium and/or antimony.

In "Chemistry letters 1989 (pp 2173-2176)" the authors have tested, in the vapour phase ammoxidation of propane, multicomponent metal oxides containing molybdenum and bismuth and exhibiting a

structure of the scheelite type. 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 some catalyst compositions tested have very little activity towards the desired reaction despite their use in conditions which lie in the explosive region or very close to the said region.

The presence of halogen compound is liable to give rise to corrosion of the equipment and is therefore not desirable in an industrial process.

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

What is more, the use of reaction mixtures lying in the explosive region is all the less desirable on an industrial scale because the process is used in a stationary bed.

It appears, therefore, that it would be highly desirable to have available a process for ammoxidation of alkanes making it possible to obtain with an appreciable selectivity a mixture of products which could be turned to profit, containing an α,β -unsaturated nitrile, in particular acrylonitrile, while reducing the losses of raw material as a result of the formation of carbon oxides.

It would also be highly desirable to have available such a process in which the solid catalyst

were relatively simple to prepare and active in the absence of a halogen-containing promoter and in the case of gas mixtures which do not necessarily lie in the explosive region.

5 The subject of the present invention is therefore a vapour phase process for ammoxidation of alkanes in the presence of a solid catalyst whose active phase contains molybdenum and oxygen, characterized in that the said active phase also
10 contains at least one element chosen from the group consisting of the alkaline-earth metals, Mn, Fe, U, La, Co, Ni, Zn, Ag, Cd, W, Zr, Pb, Te, Ga, Al, B, Nb and Ta.

 According to the present invention, acyclic
15 saturated hydrocarbons containing from 3 to 12 carbon atoms per molecule are reacted in vapour phase with ammonia and oxygen in the presence of a catalyst whose active phase has just been specified.

 Within the scope of the present process it is
20 possible, of course, to employ diluent gases which are inert under the reaction conditions, such as helium, nitrogen and argon. Similarly, water vapour can be added to the gaseous reaction mixture within wide limits. Thus, the reactive gas (saturated hydrocarbon,
25 ammonia, oxygen) can be diluted with an inert diluent and/or with water vapour. In this group the water vapour content can vary within wide limits, in particular from 0 to 50 % and preferably between 3 and

30 %. For a good use of the process according to the invention the content of reactive gas will be at least 3 % and preferably at least 20 %.

The respective contents of saturated hydrocarbon, ammonia and oxygen within the reactive gas 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 use of the process according to the invention the composition of the reactant mixture will be outside the explosive region. Where the ammoxidation of propane in the absence of inert diluent is concerned, the composition (propane, oxygen, ammonia) will be advantageously chosen within the quadrilateral ABDE which appears within the ternary diagram ABC shown in the attached single figure.

In this ternary diagram the segment AB represents the ammonia content from 100 % to 0 %; the segment BC represents the propane content from 100 to 0 %; the segment CA represents the oxygen content from 100 to 0 %. The point D, situated inside the segment BC, corresponds to a propane content of 45 %; in the binary (propane-O₂); the point E, situated inside the segment AC, corresponds to an ammonia content of 79 % in the binary (NH₃)-O₂ % [sic].

The segment DE demarcates the ternary diagram

into two parts: a triangle CDE within which the explosive region (determined at 1 bar and 25°C) is situated and a quadrilateral ABDE inside which the composition of the gaseous reactant mixture will be advantageously chosen.

Where the ammoxidation of propane in the presence of inert diluent gas(es) and/or of water vapour is concerned, it will be appropriate to determine the composition of the ternary mixture (propane, oxygen and ammonia) in order to locate it in the abovementioned diagram, when the diluent gas and/or the water vapour is/are in a low proportion.

Where the ammoxidation of propane using air as the source of oxygen is concerned, the composition (propane, air and ammonia) will be advantageously chosen inside the quadrilateral ABFG appearing within the diagram ABC shown in the attached Figure 2.

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

The segment FG demarcates the ternary diagram into two parts: a triangle CFG inside which the

explosive region (determined at 1 bar and 550°C) is situated and a quadrilateral ABFG inside which the composition of the gaseous reactant mixture will be advantageously chosen.

5 This second diagram will be employed in the case where the oxygen-diluent gas mixture corresponds to an oxygen content equivalent to that of air ($\approx 21\%$ of oxygen) or in the case where this mixture is oxygen-deficient in relation to air.

10 A mixture containing essentially propylene and acrylonitrile will be obtained by starting with propane. Acrylonitrile is an intermediate which is produced industrially on a large scale, propylene is a raw material conventionally employed for producing
15 acrylonitrile and various other intermediate products which are well known to a person skilled in the art.

 A mixture containing methacrylonitrile and isobutene or n-butenes will be obtained by starting with isobutane.

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

 While the saturated hydrocarbon used may be of technical quality, it will not contain appreciable
25 quantities of compounds with ethylenic unsaturation. Thus, the propane used will contain propylene only in trace quantities.

 The process according to the invention and

[sic] carried out in the form of vapour phase reaction. Any suitable device for carrying out vapour phase ammoxidation or oxidation reactions can consequently be employed. The process can be conducted continuously or
5 noncontinuously and may include the use of a stationary bed or of a fluidized bed.

The reaction temperature is generally between 350 and 550°C and preferably between 420 and 510°C.

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

The gas flow rate is set so that the hourly space velocity is between 100 and 36000 h⁻¹ and
15 preferably between 200 and 20000 h⁻¹ [sic].

A person skilled in the art will, of course, be capable of finding a compromise between the temperature, the gas flow rate, the precise nature of the catalyst used and the various other reaction
20 parameters, bearing in mind his production objectives.

In the process according to the present invention use is made of a solid catalyst whose active phase contains molybdenum and oxygen, the said active phase also containing at least one element chosen from
25 the group consisting of the alkaline-earth metals, Mn, Fe, U, La, Co, Ni, Zn, Ag, Cd, W, Zr, Pb, Te, Ga, Al, B, Nb and Ta.

The active phases, one of the constituents of

the catalyst used within the scope of the present invention, are molybdenum-based mixed oxides which preferably contain at least 2 elements chosen from the group defined above. Good results can be obtained
5 within the scope of the present process by the use of such an active phase containing at least one element chosen from the group consisting of the alkaline-earth metals, manganese, iron, cobalt, uranium and lanthanum.

The active phases in question are preferably
10 molybdates. The preferred active phases are manganese, uranyl, cobalt or iron molybdates.

While the proportion of element(s) M chosen from the abovementioned groups can vary within wide limits in the active phases in question, the minimum
15 will be preferably dictated by the stoichiometry of formation of the corresponding orthomolybdate. In certain cases and depending on the nature of M, a mixture of the corresponding molybdate and of a molybdenum oxide will be obtained by decreasing the
20 proportion of element(s) M.

Thus, for example, a large excess of molybdenum in relation to iron ($\text{Mo/Fe} = 10$) results in the formation of a mixture of $\text{Fe}_2(\text{MoO}_4)_3$ and of MoO_3 , the performance of which in the process in question
25 appears less good than that obtained with $\text{Fe}_2(\text{MoO}_4)_3$.

The active phases in question can be used within the scope of the process according to the invention in bulk form or in the particulate state.

These phases can be employed in the form of powders or beads which are, for example, extruded or crushed.

They can also be deposited on an inert support or may coat it. The nature of the support is not critical, provided that it is chemically inert towards the reactants under the reaction conditions which have been chosen. By way of examples of supports liable to be suitable for the preparation of catalysts which can be employed within the scope of the process according to the invention there may be mentioned: silica, alumina, silica alumina, sintered clay, carborandum [sic], magnesia, magnesium silicate and diatomaceous earth. This support is preferably nonporous and may be, in particular, based on a refractory oxide in particulate form, the most commonly employed support being clay-based. This support may, for example, consist of inert, solid, robust and rough clay beads with a diameter of between 0.5 and 6 mm. The precise value of the diameter of the beads can be chosen by a person skilled in the art as a function of the pressure drop which is permissible in the reactor. The support may also be rendered nonporous by enamelling.

The support may also be a ceramic substrate, the said substrate being preferably in the form of an inert and rigid structure of monolithic type comprising channels or conduits. Such supports are well known to a person skilled in the art and have been extensively

described in the literature. The ceramic substrates employed are especially those containing, as main substance, cordierite, alumina, mullite, porcelain and boron or silicon carbides.

5 When a coated catalyst is called for, the quantity of active phase, which may vary within wide limits, is in practice between 5 and 35 % and preferably between 10 and 15 % by weight relative to the total (support + active phase).

10 The preparation of the catalysts used in the process according to the invention can be carried out in various ways which are known per se, such as mixing appropriate salts of the elemental constituents in water or in another solvent, followed by evaporation to
15 dryness, or by precipitation by adding a base such as aqueous ammonia or an acid such as hydrochloric acid, or by spraying a suspension obtained after mixing suitable salts.

 The suitable salts most commonly employed are
20 soluble in water and contain anions and cations which can be decomposed by heat during subsequent stages. They are, for example, ammonium heptamolybdate in the case of molybdenum, and alkaline-earth metal, manganese, iron, cobalt, uranium, lanthanum, etc.
25 nitrates or chlorides in the case of metals.

 Once the mixture of the salts has been produced, a precursor can be obtained by the so-called evaporation method. The water in the suspension

obtained is evaporated off by heating between 20 and 100°C with stirring for the time needed to obtain a paste which does not run. Stirring and heating are then stopped.

5 The paste thus obtained, spread out into a thickness of approximately 2 cm, is dried in air at approximately 120°C for approximately 15 h. The precursor thus obtained can then be ground and calcined between 200 and 1000°C, preferably between 400 and 10 600°C, for at least 30 min, preferably at least one hour. The calcination may be performed by progressively raising the temperature, for example 100 to 200°C per hour, in particular owing to the risks related to the exothermic decomposition of ammonium nitrate at about 15 230°C. The active phase thus obtained after cooling can then be ground in order that its particle size should not exceed approximately 400 μm .

 The precursor can also be obtained by an alternative method comprising precipitation with the 20 addition, for example, of aqueous ammonia or of hydrochloric acid at the end of mixing of the salts, to stabilise the pH at approximately 7. It is preferable to heat the suspension between 20 and 100°C for approximately one hour to complete the precipitation of 25 the species.

 The suspension is then filtered and washed. The filter cake is next spread out and then dried, ground and calcined according to the conditions

described above within the scope of the evaporation method, to give the active phase.

Certain catalysts which are useful for an application of the process in a stationary bed, can be
5 obtained by coating, in a manner known per se, of ground, intermediate or finished, active phases. This traditional method consists in depositing a layer of intermediate or finished active phase around inert but rough beads.

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

Some catalysts which are useful for an application of the process according to the invention in a stationary bed or fluidized bed can be obtained by the technique, known per se, of spray-drying in a
20 preferably nonreducing atmosphere. Using such an operation, if appropriate followed by a calcination at a temperature of the order of 400 to 1100°C, powders of spherical form with a diameter of between 5 and 700 μm are obtained. Powders which comprise at least 80 % by
25 weight of particles which are between 5 and 100 μm in size are preferred within the scope of a utilisation in a fluidized bed.

The reaction products can be recovered in the

effluent gases by any appropriate means. For example, the effluent gases may pass through a condenser containing dilute sulphuric acid to neutralize the unconverted ammonia. The gases may then pass through a refrigerated absorbing column to condense the acrylonitrile, acetonitrile and hydrocyanic acid, the uncondensed vapour containing chiefly unconverted propane propylene, light hydrocarbons and, where applicable, CO_2 . Acrylonitrile and hydrocyanic acid can then be separated from acetonitrile by distillation and the recovered acrylonitrile-hydrocyanic acid mixture can then itself be distilled to separate acrylonitrile from hydrocyanic acid.

The examples below illustrate the present invention.

EXAMPLE 1 : PREPARATION OF A CATALYST BASED ON MAGNESIUM MOLYBDATE :

A solution (a) of ammonium heptamolybdate is prepared by dissolving 52.98 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (marketed by Merck) in 200 cm³ of demineralized water (pH of the solution obtained: 5-6), and a solution (b) of magnesium nitrate by dissolving 79.3 g of 97% $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (marketed by Prolabo) in 200 cm³ of demineralized water. The solution (b) is added to the solution (a) in a stirred reactor (pH = 5). The mixture is heated on a hotplate and the paste obtained is dried at 120°C for approximately 15 h; the product obtained is then ground in a mortar and calcined in air at 500°C

for 4 h.

The product (I) thus prepared has the composition MgMoO_4 , identified by X-ray diffraction, and has a specific surface, measured by the B.E.T. method, of $5 \text{ m}^2 \text{ g}^{-1}$.

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

The catalyst (A) thus obtained consists of 12 % by weight of MgMoO_4 deposited on clay beads.

EXAMPLE 2 - PREPARATION OF A CATALYST BASED ON MANGANESE MOLYBDATE -

An active phase of composition MnMoO_4 is prepared using the operating procedure described by U. Ozran, R. C. Gill and M. R. Smith, J. Catal. 116, 171-183 (1989).

A solution (a) of ammonium heptamolybdate is prepared by dissolving 70.64 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (marketed by Merck) in 200 cm³ of demineralized water, and a solution (b) of manganese chloride by dissolving

79.16 g of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (marketed by Prolabo) in 400 cm³ of demineralized water. The solution (a) is added dropwise to the solution (b) in an energetically stirred reactor. Heating to 80°C is applied and the pH is maintained at 6 by adding dilute hydrochloric acid or aqueous ammonia (both marketed by Prolabo) for 3 h. The material is filtered hot on sintered glass and washed with 1 l of demineralized water. The product obtained is then dried at 120°C for approximately 15 h, ground in a mortar, and calcined in air at 500°C for 4 h.

The product (I) thus prepared has the composition MnMoO_4 , identified by X-ray diffraction, and has a specific surface, measured by the B.E.T. method, of $5\text{m}^2\text{g}^{-1}$ [sic].

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

The catalyst (B) thus obtained consists of 11 % by weight of MnMoO_4 deposited on clay beads.

EXAMPLE 3 - PREPARATION OF ANOTHER CATALYST BASED ON
MANGANESE MOLYBDATE. -

20 g of product (I) of composition MnMoO_4 as described in the preceding example are prepared. This
5 product is then compressed under a pressure of 20 t. Tablets 3 cm in diameter and approximately 0.5 cm in thickness are thus obtained. These tablets are then crushed into fragments with a particle size of between 0.3 and 0.8 cm, constituting the catalyst (C).

10 EXAMPLE 4 - PREPARATION OF A CATALYST BASED ON
URANYL MOLYBDATE :

An active phase of composition UO_2MoO_4 is prepared by the operating procedure described by E. Bordes, State Thesis, Compiègne (1979).

15 A solution (a) of ammonium heptamolybdate is prepared by dissolving 35.32 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (marketed by Merck) in 200 cm³ of demineralized water, and a solution (b) of uranyl nitrate by dissolving 100.43 g of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (marketed by Prolabo) in
20 200 cm³ of demineralized water. The solution (b) is added to the solution (a) in a stirred reactor. 100 cm³ of demineralized water are added, the mixture is heated on a hotplate and the paste obtained is dried at 120°C for approximately 15 h; the product obtained is then
25 ground in a mortar and calcined in air at 550°C for 12 h.

The product (I) thus prepared has the composition UO_2MoO_4 , identified by X-ray diffraction,

and has a specific surface, measured by the B.E.T. method, of $2.7 \text{ m}^2 \text{ g}^{-1}$.

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

The catalyst (D) thus obtained consists of 11 % by weight of UO_2MoO_4 deposited on clay beads.

EXAMPLE 5 - PREPARATION OF A CATALYST BASED ON CALCIUM MOLYBDATE :

A solution (a) of ammonium heptamolybdate is prepared by dissolving 52.98 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (marketed by Merck) in 200 cm³ of demineralized water, and a solution (b) of calcium nitrate by dissolving 47.23 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (marketed by Prolabo) in 200 cm³ of demineralized water. The solution (b) is added to the solution (a) in a stirred reactor. The pH of the mixture, initially 4.5, is raised to 6.7 by adding aqueous ammonia (marketed by Prolabo). Heating is carried out on a hotplate and the paste obtained is dried at 120°C for approximately 15 h; the product

obtained is then ground in a mortar and calcined in air at 500°C for 7 h.

The product (I) thus prepared has the composition CaMoO_4 , identified by X-ray diffraction, and has a specific surface, measured by the B.E.T. method, of $5\text{m}^2\text{g}^{-1}$.

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

The catalyst (E) thus obtained consists of 11 % by weight of CaMoO_4 deposited on clay beads.

20 EXAMPLE 6 - PREPARATION OF A CATALYST BASED ON MIXED MOLYBDENUM LANTHANUM OXIDE -

A solution (a) of ammonium heptamolybdate is prepared by dissolving 35.32 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (marketed by Merck) in 200 cm³ of demineralized water, and a solution (b) of lanthanum nitrate by diluting 71.64 cm³ of $\text{La}(\text{NO}_3)_3$ containing 455 g l⁻¹ as La_2O_3 (source: Rhone-Poulenc factory in La Rochelle) in 200 cm³ of demineralized water. The solution (a) is

added to the solution (b) in a stirred reactor. The mixture is acidified to pH = 1-2 by adding concentrated nitric acid. Heating is carried out on a hotplate at 100-110°C and the paste obtained is dried at 120°C for approximately 15 h; the product obtained is then ground in a mortar and calcined in air at 500°C for 3 h.

The product (I) thus prepared consists of a mixture of lanthanum and molybdenum oxides, identified by X-ray diffraction, and has a specific surface, measured by the B.E.T. method, of $6\text{m}^2\text{g}^{-1}$.

20 g of the product (I) are sprinkled slowly onto 123 g of inert support consisting of clay beads with a mean diameter of 4.8 mm, placed beforehand in a rotating pelletizer and moistened with glucose in aqueous solution at a concentration of 10 %. As soon as the beads are dry outside, a small quantity of the glucose solution is sprayed. The product (I) is then again sprinkled onto the beads. These operations are continued alternately until all of the product (I) is coated. Drying is then carried out at 120°C for 2 h and calcining at 480°C for 6 h.

The catalyst (F) thus obtained consists of 9 % by weight of LaMoO_x deposited on clay beads.

EXAMPLE 7 - PREPARATION OF A CATALYST BASED ON IRON MOLYBDATE -

An active phase of composition $\text{Fe}_2(\text{MoO}_4)_3$ is prepared by the operating procedure described by S. Nasu and S. Shimizu, J. Catal. 104, 164-175 (1987).

A solution (a) of ammonium heptamolybdate is prepared by dissolving 52.98 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (marketed by Merck) in 200 cm³ of demineralized water, and a solution (b) of iron nitrate by dissolving 80.8 g of $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (marketed by Prolabo) in 200 cm³ of demineralized water. The solution (b) is added to the solution (a) in a stirred reactor. The pH of the mixture is adjusted to 7.5 by adding aqueous ammonia (marketed by Prolabo). Heating is applied on a hotplate and the paste obtained is dried at 120°C for approximately 15 h; the product obtained is then ground in a mortar and calcined in air at 500°C for 1 h and reground and recalcined in air at 500°C for 1 h.

The product (I) thus prepared has the composition $\text{Fe}_2(\text{MoO}_4)_3$, identified by X-ray diffraction, and has a specific surface, measured by the B.E.T. method, of $3.9\text{m}^2\text{g}^{-1}$.

20 g of the product (I) are sprinkled slowly onto 123 g of inert support consisting of clay beads with a mean diameter of 4.8 mm, placed beforehand in a rotating pelletizer and moistened with glucose in aqueous solution at a concentration of 10 %. As soon as the beads are dry outside, a small quantity of the glucose solution is sprayed. The product (I) is then again sprinkled onto the beads. These operations are continued alternately until all of the product (I) is coated. Drying is then carried out at 120°C for 2 h and calcining at 480°C for 6 h.

The catalyst (G) thus obtained consists of 13 % by weight of $\text{Fe}_2(\text{MoO}_4)_3$ deposited on clay beads.

EXAMPLE 8 - PREPARATION OF A CONTROL CATALYST BASED ON MIXED MOLYBDENUM TIN OXIDE -

5 (This catalyst does not come within the scope of the invention).

A solution (a) of ammonium heptamolybdate is prepared by dissolving 35.32 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (marketed by Merck) in 200 cm³ of demineralized water, and a solution (b) of tin chloride by dissolving 45.13 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (marketed by Prolabo) in 200 cm³ of demineralized water, acidified with a few drops of concentrated hydrochloric acid. The solution (b) is added to the solution (a) in a stirred reactor. The mixture is heated and aqueous ammonia (marketed by Prolabo) is added to neutral pH. The material is filtered on sintered glass and washed with 100 cm³ of demineralized water; the product obtained is dried at 120°C for approximately 15 h, ground in a mortar and calcined in air at 500°C for 3 h.

The product (I) thus prepared has the composition $\text{SnO}_2 \cdot 2\text{MoO}_3$, identified by X-ray diffraction, and has a specific surface, measured by the B.E.T. method, of 26 m²g⁻¹.

25 20 g of the product (I) are sprinkled slowly onto 123 g of inert support consisting of clay beads with a mean diameter of 4.8 mm, placed beforehand in a rotating pelletizer and moistened with glucose in

aqueous solution at a concentration of 10 %. As soon as the beads are dry outside, a small quantity of the glucose solution is sprayed. The product (I) is then again sprinkled onto the beads. These operations are continued alternately until all of the product (I) is coated. Drying is then carried out at 120°C for 2 h and calcining at 480°C for 6 h.

The catalyst (H) thus obtained consists of 11 % by weight of $\text{SnO}_2\text{-2MoO}_3$ deposited on clay beads.

10 EXAMPLE 9 - PREPARATION OF A CATALYST BASED ON
MANGANESE MOLYBDATE AND ALUMINA
(30-70 % wt)

A solution (a) is prepared by dissolving 26.47 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ in 120 cm³ of demineralized water, and a solution (b) by dissolving 37.65 g of $\text{Mn}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ in 60 cm³ of demineralized water and a suspension (c) of 75.2 g of alumina in 100 cm³ of demineralized water. The solution (a) is added to the solution (c) and the solution (b) is then added. Stirring is carried out for 2 h and the material is evaporated to dryness. It is then dried at 120°C and calcined 500°C for 4 h. A product (I) is thus obtained.

20 g of the product (I) are sprinkled slowly onto 123 g of inert support consisting of clay beads with a mean diameter of 4.8 mm, placed beforehand in a rotating pelletizer and moistened with glucose in aqueous solution at a concentration of 10 %. As soon as the beads are dry outside, a small quantity of the

glucose solution is sprayed. The product (I) is then again sprinkled onto the beads. These operations are continued alternately until all of the product (I) is coated.

5 Drying is then carried out at 120°C for 2 h and calcining at 480°C for 6 h. The catalyst (J) thus obtained consists of 11 % by weight of $\text{MnMoO}_4\text{-Al}_2\text{O}_3$ (30-70 wt %) deposited on clay beads.

EXAMPLE 10 - PREPARATION OF A CATALYST BASED ON
10 MANGANESE MOLYBDATE AND SILICA -

A solution (a) is prepared by dissolving 58.3 g of $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$ and 8.2 g of MoO_3 in 150 cm³ of demineralized water at 50-60°C. A solution (b) is prepared by dissolving 100.4 g of $\text{Mn}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ in
15 100 cm³ of demineralized water. The solution (b) is added to the solution (a) at room temperature.

31.9 cm³ extended to 40 cm³ of the solution obtained are then impregnated dry onto 50 g of silica beads. Drying is then carried out at 120°C for
20 approximately 15 h and calcining at 500°C for 4 h.

The catalyst (K) thus obtained consists of 14.6 % by weight of MnMoO_4 deposited on silica.

GENERAL OPERATING PROCEDURE FOR THE AMMOXIDATION TESTS

25 The catalyst sample is preheated on a measuring bench to a temperature of 150°C under helium blanketing for 10 min and is then subjected to a gas flow whose composition will be specified for each

example and which contains propane, ammonia, oxygen, water vapour and helium.

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

The gas flow rate is defined so as to give an hourly space velocity (HSV) of between 100 and 36000 h⁻¹, the precise value of which will be shown for each example.

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

- The catalyst is heated to a temperature T_1 , for example 300°C, and after 30 min of stabilization at the temperature T_1 the composition of the mixture
15 leaving the reactor is determined by gas phase chromatography.

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

Propane conversion = % propane converted/% propane introduced

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

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

The following conventions are employed in the examples below:

	DCC3H8	=	propane conversion
	SACN	=	selectivity for acrylonitrile
5	SACN+C ₃ H ₆	=	selectivity for acrylonitrile and propylene
	SCOX	=	selectivity for carbon monoxide and dioxide.

EXAMPLES 11 TO 13 -

10 Measurement of the performance of catalysts
(A), (B) and (D).

The operating conditions used are the following:

	Hourly space velocity = 1000 h ⁻¹	
15	Total pressure	= 1.3 bar
	Composition of the reaction mixture:	
	C ₃ H ₈	= 11 %
	NH ₃	= 7.5 %
	O ₂	= 10 %
20	H ₂ O	= 25 %
	He	= 46.5 %

The results and the particular conditions appear in Table I below:

TABLE I

EXAMPLES	CATALYST	T°C	DCC3H8 (%)	SACN (%)	SACN+ C3H6 (%)	SCOX (%)
11	(A)	470	6	10	73	0
12	(B)	470 510	2 5.5	1 19	98 77	0 0
13	(D)	470 510	3 5	15 14	44 71	0 0

EXAMPLES 14 TO 16; control test a:

Measurement of the performance of catalysts (E) to (H).

The operating conditions used are the following:

Hourly space velocity = 1000 h^{-1}

Total pressure = 1.3 bar

Composition of the reaction mixture:

C_3H_8 = 30 %

NH_3 = 15 %

O_2 = 15 %

H_2O = 20 %

He = 20 %

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

TABLE II

EXAMPLES	CATALYST	T°C	DCC3H8 (%)	SACN (%)	SACN+ C3H6 (%)	SCOX (%)
5	(E)	475	2	0	78	0
		490	4	9.5	69	0
10	(F)	460	1	3	83	0
		490	7	19	55	0
		510	7.5	10	60	6
10	(G)	460	5	20	59	0
		475	7	23	56	0
		490	6	19	58	13
15	(H)	440	9	6	32	19
		460	11	20	43	16
		475	11	24	47	13

15 EXAMPLES 17 TO 19 -

Measurement of the performance of catalyst
(A) at different partial pressures of propane.

The operating conditions used are the
following:

20 Temperature = 510°C

Hourly space velocity = 1000 h⁻¹

Total pressure = 1.3 bar

Composition of the reaction mixture:

25 C₃H₈ = 11 % or 19 or 26 %

NH₃ = 7.5 %

O₂ = 10 %

H₂O = 25 %

He = 31.5 % or 38.5 or 46.5 %

The results and the particular conditions
30 appear in Table III below:

TABLE III

EXAMPLES	C ₃ H ₈ (%)	DCC ₃ H ₈ (%)	SACN (%)	SACN+ C ₃ H ₆ (%)	SCOX (%)
17	11	17	3	50	21
18	19	16	16	69	5
19	26	16	13	72	5.5

EXAMPLES 20 TO 23 -

Measurement of the performance of catalyst
(B) at different temperatures.

The operating conditions used are the
following:

Hourly space velocity = 1000 h⁻¹

Total pressure = 1.3 bar

Composition of the reaction mixture:

C₃H₈ = 19 %

NH₃ = 7.5 %

O₂ = 10 %

H₂O = 25 %

He = 38.5 %

The results and the particular conditions
appear in Table IV below:

TABLE IV

EXAMPLES	T°C	DCC3H8 (%)	SACN (%)	SACN+ C3H6 (%)	SCOX (%)
20	420	0.4	16	81	0
21	470	2	17	72	0
22	485	3	17	71	0
23	510	8	30	67	0

EXAMPLE 24 TO 26 :

Measurement of the performance of catalyst
(B) at different hourly space velocities.

The operating conditions used are the following:

Temperature = 510°C

Total pressure = 1.3 bar

Composition of the reaction mixture:

C_3H_8 = 19 %

NH_3 = 7.5 %

O_2 = 10 %

H_2O = 25 %

He = 38.5 %

The particular conditions and the results obtained appear in Table V below:

TABLE V

EX- AMPLES	HSV (h-1)	Volcata (ml)	DCC3H8 (%)	SACN (%)	SACN+ C3H6 (%)	SCOX (%)
24	200	100	13	21	77	2
25	500	40	13	27	65	0
26	1000	20	8	30	67	0

EXAMPLES 27 TO 31 -

Measurement of the performance of catalyst
(B) at different temperatures.

The operating conditions used are the
following:

Hourly space velocity = 500 h^{-1}

Total pressure = 1.3 bar

Composition of the reaction mixture:

$\text{C}_3\text{H}_8 = 19 \%$

$\text{NH}_3 = 7.5 \%$

$\text{O}_2 = 10 \%$

$\text{H}_2\text{O} = 25 \%$

$\text{He} = 38.5 \%$

The results and the particular conditions
appear in Table VI below:

TABLE VI

EXAMPLES	T°C	DCC3H8 (%)	SACN (%)	SACN+ C3H6 (%)	SCOX (%)
27	420	1	3	87	0
28	450	3	15	58	0
29	470	5	20	62	0
30	490	9	27	62	0
31	510	13	27	65	0

EXAMPLES 32 TO 36 :

10 Measurement of the performance of catalyst
(C) at different temperatures.

The operating conditions used are the
following:

Hourly space velocity = 1000 h^{-1}

15 Total pressure = 1.3 bar

Composition of the reaction mixture:

C_3H_8 = 19 %

NH_3 = 7.5 %

O_2 = 10 %

20 H_2O = 25 %

He = 38.5 %

The particular conditions and the results
obtained appear in Table VII below:

TABLE VII

EXAMPLES	T°C	DCC3H8 (%)	SACN (%)	SACN+ C3H6 (%)	SCOX (%)
32	410	3	9	64	0
33	430	6	13	74	0
34	470	11	16	76	4
35	490	20	23	73	9
36	510	24	24	73	6

EXAMPLES 37 TO 39 :

10 Measurement of the performance of catalyst
(B) at different partial pressures of propane.

The operating conditions used are the
following:

15 Temperature = 510°C
Hourly space velocity = 1000 h⁻¹
Total pressure = 1.3 bar
Composition of the reaction mixture:
C₃H₈ = 11 % or 19 or 26 %
NH₃ = 7.5 %
20 O₂ = 10 %
H₂O = 25 %
He = 31.5 % or 38.5 or 46.5 %

The particular conditions and the results
obtained appear in Table VIII below:

TABLE VIII

EXAMPLES	C3H8 (%)	DCC3H8 (%)	SACN (%)	SACN+ C3H6 (%)	SCOX (%)
37	11	5	19	77	0
38	19	8	30	67	0
39	26	5	13	80	0

EXAMPLES 40 TO 42 -

Measurement of the performance of catalyst
(B) at different partial pressures of ammonia.

The operating conditions used are the
following:

Temperature = 510°C

Hourly space velocity = 1000 h⁻¹

Total pressure = 1.3 bar

Composition of the reaction mixture:

C₃H₈ = 19 %

NH₃ = 4 % or 7.5 or 11 %

O₂ = 10 %

H₂O = 25 %

He = 35 % or 38.5 or 42 %

The particular conditions and the results
obtained appear in Table IX below:

TABLE IX

EXAMPLES	NH ₃ (%)	DCC ₃ H ₈ (%)	SACN (%)	SACN+ C ₃ H ₆ (%)	SCOX (%)
40	4	4	0	82	17
41	7.5	8	30	67	0
42	11	10	30	60	0

EXAMPLE 43 TO 45 :

Measurement of the performance of catalyst

(D) at different partial pressures of propane.

The operating conditions used are the following:

Temperature = 510°C

Hourly space velocity = 1000 h⁻¹

Total pressure = 1.3 bar

Composition of the reaction mixture:

C₃H₈ = 11 % or 19 or 26 %

NH₃ = 7.5 %

O₂ = 10 %

H₂O = 25 %

He = 31.5 % or 38.5 or 46.5 %

The particular conditions and the results obtained appear in Table X below:

TABLE X

EXAMPLES	C ₃ H ₈ (%)	DCC ₃ H ₈ (%)	SACN (%)	SACN+ C ₃ H ₆ (%)	SCOX (%)
43	11	5	14	71	0
44	19	4	11	73	0
45	26	7	22	54	0

EXAMPLE 46 TO 48 -

Measurement of the performance of catalyst
(D) at different partial pressures of ammonia.

The operating conditions used are the
following:

Temperature = 510°C

Hourly space velocity = 1000 h⁻¹

Total pressure = 1.3 bar

Composition of the reaction mixture:

C₃H₈ = 19 %

NH₃ = 4 % or 7.5 or 11 %

O₂ = 10 %

H₂O = 25 %

He = 35 % or 38.5 or 42 %

The particular conditions and the results
obtained appear in Table XI below:

TABLE XI

EXAMPLES	NH ₃ (%)	DCC ₃ H ₈ (%)	SACN (%)	SACN+ C ₃ H ₆ (%)	SCOX (%)
46	4	6	24	62	0
47	7.5	4	11	73	0
48	11	4	13	70	0

EXAMPLE 49 TO 51 :

Measurement of the performance of catalyst
(F) at different partial pressures of oxygen.

The operating conditions used are the
following:

Temperature = 490°C

Hourly space velocity = 1000 h⁻¹

Total pressure = 1.3 bar

Composition of the reaction mixture:

C₃H₈ = 20 %

NH₃ = 15 %

O₂ = 5 % or 15 or 25 %

H₂O = 20 %

He = 20 % or 30 or 40 %

The particular conditions and the results
obtained appear in Table XII below:

TABLE XII

EXAMPLES	O ₂ (%)	DCC ₃ H ₈ (%)	SACN (%)	SACN+ C ₃ H ₆ (%)	SCOX (%)
49	5	4	15	63	0
50	15	6	14	59	0
51	25	8	18	58	4

EXAMPLES 52 AND 53 :

Measurement of the performance of catalyst
(G) at different partial pressures of ammonia.

The operating conditions used are the
following:

Temperature = 490°C

Hourly space velocity = 1000 h⁻¹

Total pressure = 1.3 bar

Composition of the reaction mixture:

C₃H₈ = 20 %

NH₃ = 5 % or 25 %

O₂ = 5 %

H₂O = 20 %

He = 20 % or 40 %

The particular conditions and the results
obtained appear in Table XIII below:

TABLE XIII

EXAMPLES	NH ₃ (%)	DCC3H ₈ (%)	SACN (%)	SACN+ C ₃ H ₆ (%)	SCOX (%)
52	5	12	17	45	28
53	25	14	7	42	4

EXAMPLES 54 AND 55 :

Measurement of the performance of catalyst
(G) at different partial pressures of oxygen.

The operating conditions used are the
following:

Temperature = 475°C

Hourly space velocity = 1000 h⁻¹

Total pressure = 1.3 bar

Composition of the reaction mixture:

C₃H₈ = 20 %
NH₃ = 15 %
O₂ = 5 % or 25 %
H₂O = 20 %
He = 20 % or 40 %

The particular conditions and the results
obtained appear in Table XIV below:

TABLE XIV

EXAMPLES	O ₂ (%)	DCC3H ₈ (%)	SACN (%)	SACN+ C ₃ H ₆ (%)	SCOX (%)
54	5	8	15	58	4
55	25	11	17	60	14

EXAMPLES 56 AND 57 :

Measurement of the performance of catalyst
(J) and (K).

The operating conditions used are the
5 following:

Hourly space velocity = 1000 h⁻¹

Total pressure = 1.3 bar

Composition of the reaction mixture:

10 C₃H₈ = 48 %
NH₃ = 95 %
O₂ = 18 %
H₂O = 20 %
He = 5 %

The particular conditions and the results
15 obtained appear in Table XV below:

TABLE XV

EXAMPLES	CATALYST	T°C	DCC3H8 (%)	SACN (%)	SACN+ C3H6 (%)	SCOX (%)
56	(J)	500	15	15	62	0
20 57	(K)	460	12	14	37	0.2

Control tests b, c, d:

Measurement of the performance of catalyst
(H) at different temperatures.

The operating conditions used are the
25 following:

Hourly space velocity = 1000 h^{-1}

Total pressure = 1.3 bar

Composition of the reaction mixture:

$\text{C}_3\text{H}_8 = 20 \%$

5 $\text{NH}_3 = 5 \%$

$\text{O}_2 = 15 \%$

$\text{H}_2\text{O} = 20 \%$

$\text{He} = 40 \%$

The particular conditions and the results
10 obtained appear in Table XVI below:

TABLE XVI

EXAMPLES	T°C (%)	DCC3H8 (%)	SACN (%)	SACN+ C3H6 (%)	SCOX (%)
b	460	19	13	25	38
15 c	475	20	19	32	43
d	490	21	26	41	28

EXAMPLE 58 - PREPARATION OF A CATALYST BASED ON
URANYL MOLYBDATE

An active phase of composition $\text{UMo}_{10}\text{O}_x$ is
20 prepared according to the following operating
procedure.

A solution (a) of ammonium heptamolybdate is
prepared by dissolving 176.56 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$
(marketed by Merck) in 400 cm³ of demineralized water,
25 and a solution (b) of uranyl nitrate by dissolving
50.2 g of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (marketed by Prolabo) in 50 cm³

of demineralized water. The solution (b) is added to the solution (a) in a stirred reactor and is heated to approximately 80°C. The material is kept at 80-100°C for approximately 2 hours and the paste obtained is
5 dried at 120°C for approximately 15 h; the product obtained is then calcined in air at 500°C for 4 h.

The product thus prepared has a specific surface, measured by the B.E.T. method, of 2.4 m²g⁻¹.

10 g of this product are sprinkled slowly
10 onto 65 g of inert support consisting of clay beads with a mean diameter of 4.8 mm, placed beforehand in a rotating pelletizer and moistened with glucose in aqueous solution at a concentration of 10 %. As soon as the beads are dry outside, a small quantity of the
15 glucose solution is sprayed. The product is then again sprinkled onto the beads. These operations are continued alternately until all the product is coated. Drying is then carried out at 120°C for 2 h and calcining at 480°C for 6 h.

20 The catalyst (L) thus obtained consists of 11.2 % by weight of UMo₁₀O_x deposited on clay beads.

EXAMPLE 59 - PREPARATION OF A CATALYST BASED ON
COBALT MOLYBDATE

An active phase of composition CoMoO₄ is
25 prepared using the following operating procedure.

A solution (a) of ammonium heptamolybdate is prepared by dissolving 70.6 g of (NH₄)₆Mo₇O₂₄·4H₂O (marketed by Merck) in 400 cm³ of demineralized water,

and a solution (b) of cobalt nitrate by dissolving 116.4 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 150 cm³ of demineralized water. Solution (b) is added to the solution (a) in a stirred reactor and is heated to boiling. The paste
5 obtained is dried at 120°C for approximately 15 h and is then calcined in air at 500°C for 4 h.

The product thus prepared has a specific surface, measured by the B.E.T. method, of 7.7 m²g⁻¹.

10 g of this product are sprinkled slowly
10 onto 50 g of inert support, consisting of clay beads with a mean diameter of 4.8 mm, placed beforehand in a rotating pelletizer and moistened with glucose in aqueous solution at a concentration of 10 %. As soon as the beads are dry outside, a small quantity of the
15 glucose solution is sprayed. The product is then again sprinkled onto the beads. These operations are continued alternately until all the product is coated. Drying is then carried out at 120°C for 2 h and calcining at 480°C for 6 h.

20 The catalyst (M) thus obtained consists of 11.7 % by weight of CoMoO_4 deposited on clay beads.

EXAMPLE 60 - PREPARATION OF A CATALYST BASED ON
COBALT MOLYBDATE

An active phase of composition CoMoO_4 is
25 prepared using the following operating procedure.

A solution (a) of ammonium heptamolybdate is prepared by dissolving 70.6 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (marketed by Merck) in 400 cm³ of demineralized water,

and a solution (b) of cobalt nitrate by dissolving 116.4 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 150 cm³ of demineralized water. Solution (b) is added to the solution (a) in a stirred reactor and is heated to boiling. The paste
5 obtained is filtered on sintered glass, dried at 120°C for approximately 15 h and is then calcined in air at 500°C for 4 h.

The product thus prepared has a specific surface, measured by the B.E.T. method, of 13 m²g⁻¹.

10 10 g of this product are sprinkled slowly onto 67 g of inert support, consisting of clay beads with a mean diameter of 4.8 mm, placed beforehand in a rotating pelletizer and moistened with glucose in aqueous solution at a concentration of 10 %. As soon as
15 the beads are dry outside, a small quantity of the glucose solution is sprayed. The product is then again sprinkled onto the beads. These operations are continued alternately until all the product is coated. Drying is then carried out at 120°C for 2 h and
20 calcining at 480°C for 6 h.

The catalyst (N) thus obtained consists of 10 % by weight of CoMoO_4 deposited on clay beads.

EXAMPLES 61 TO 65 -

Measurement of the performance of catalyst
25 (L) at different temperatures and with different compositions of the reaction mixture.

The operating conditions used are the following:

Hourly space velocity = 1000 h^{-1}

Total pressure = 1.3 bar

The composition of the reaction mixture, the temperature and the results obtained appear in Table

5 XVII below.

TABLE XVII

	EXAMPLES	61	62	63	64	65
	C_3H_8 (% vol)	7.5	25	25	40	48
	NH_3 (% vol)	15	25	10	15	9
10	O_2 (% vol)	15	10	25	15	18
	He (% vol)	42.5	20	20	10	5
	T ($^{\circ}\text{C}$)	460	430	460	460	480
	DCC_3H_8 (%)	4	2	5	3	6
	SACN (%)	19	15	13	13	18
15	SACN + C_3H_6 (%)	48	59	32	78	44
	SCO_x (%)	0	0	0	1	0

EXAMPLES 66 TO 69:

Measurement of the performance of catalyst (M) at different temperatures and with different
20 compositions of the reaction mixture.

The operating conditons used are the following:

Hourly space velocity = 1000 h^{-1}

Total pressure = 1.3 bar

25 The composition of the reaction mixture, the temperature and the results obtained appear in Table XVIII below.

TABLE XVIII

5	EXAMPLES	66		67		68		69		
	C ₃ H ₈ (% vol)	7.5		25		40		48		
	NH ₃ (% vol)	15		25		15		9		
	O ₂ (% vol)	15		10		15		18		
	He (% vol)	42.5		20		10		5		
10	T (°C)	460	480	460	480	460	480	440	460	480
	DCC ₃ H ₈ (%)	8	17	6	6	7	11	6	10	16
	SACN (%)	20	31	14	12	13	17	16	18	17
	SACN + C ₃ H ₆ (%)	76	75	59	67	83	84	73	79	75
	SCOx (%)	0	0	0	0	0	1	0	1	5

EXAMPLES 70 TO 73:

Measurement of the performance of catalyst
(N) at different temperatures and with different
15 compositions of the reaction mixture.

The operating conditons used are the
following:

Hourly space velocity = 1000 h⁻¹

Total pressure = 1.3 bar

20 The composition of the reaction mixture, the
temperature and the results obtained appear in Table
XIX below.

TABLE XIX

5	EXAMPLES	70	71		72		73
	C_3H_8 (% vol)	7.5	25		40		48
	NH_3 (% vol)	15	10		15		9
	O_2 (% vol)	15	25		15		18
	He (% vol)	42.5	20		10		5
10	T ($^{\circ}C$)	480	460	480	440	460	440
	DCC_3H_8 (%)	11	8	15	6	11	5
	SACN (%)	14	17	20	11	17	12
	SACN + C_3H_6 (%)	84	82	76	83	83	82
	SCOx (%)	2	0	4	0	1	0



CLAIMS

1. Process for ammoxidation of alkanes in vapour phase in the presence of a solid catalyst whose active phase contains molybdenum and oxygen,
5 characterized in that the said active phase also contains at least one element chosen from the group consisting of the alkaline-earth metals, Mn, Fe, U, La, Co, Ni Zn, Ag, Cd, W, Zr, Pb, Te, Ga, Al, B, Nb and Ta.
2. Process according to Claim 1,
10 characterized in that the said active phase contains at least 2 elements chosen from the group defined above.
3. Process according to Claim 1,
characterized in that the said active phase contains at least one element chosen from the group consisting of
15 the alkaline-earth metals, manganese, iron, cobalt, uranium and lanthanum.
4. Process according to any one of the preceding claims, characterized in that the said active phase is a mixed oxide based on molybdenum.
- 20 5. Process according to any one of Claims 1 to 3, characterized in that the said active phase is an orthomolybdate.
6. Process according to Claim 5,
characterized in that the said active phase is a
25 manganese, uranyl, cobalt or iron molybdate.
7. Process according to any one of the preceding claims, characterized in that the alkane is



propane.

8. Process according to any one of the preceding claims, characterized in that the reaction is conducted in the presence of water vapour.

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

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

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

15 12. Process according to any one of the preceding claims, characterized in that in the reactant gas (mixture of saturated hydrocarbon, ammonia and oxygen) the saturated hydrocarbon content is between 5 and 70 %, the ammonia content is between 3 and 50 % and the oxygen content is between 3 and 45 %.

20 13. Process according to any one of the preceding claims, characterized in that the composition of the gaseous mixture is outside the explosive region.

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

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PROCESS FOR AMMOXIDATION OF SATURATED HYDROCARBONS

ABSTRACT

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

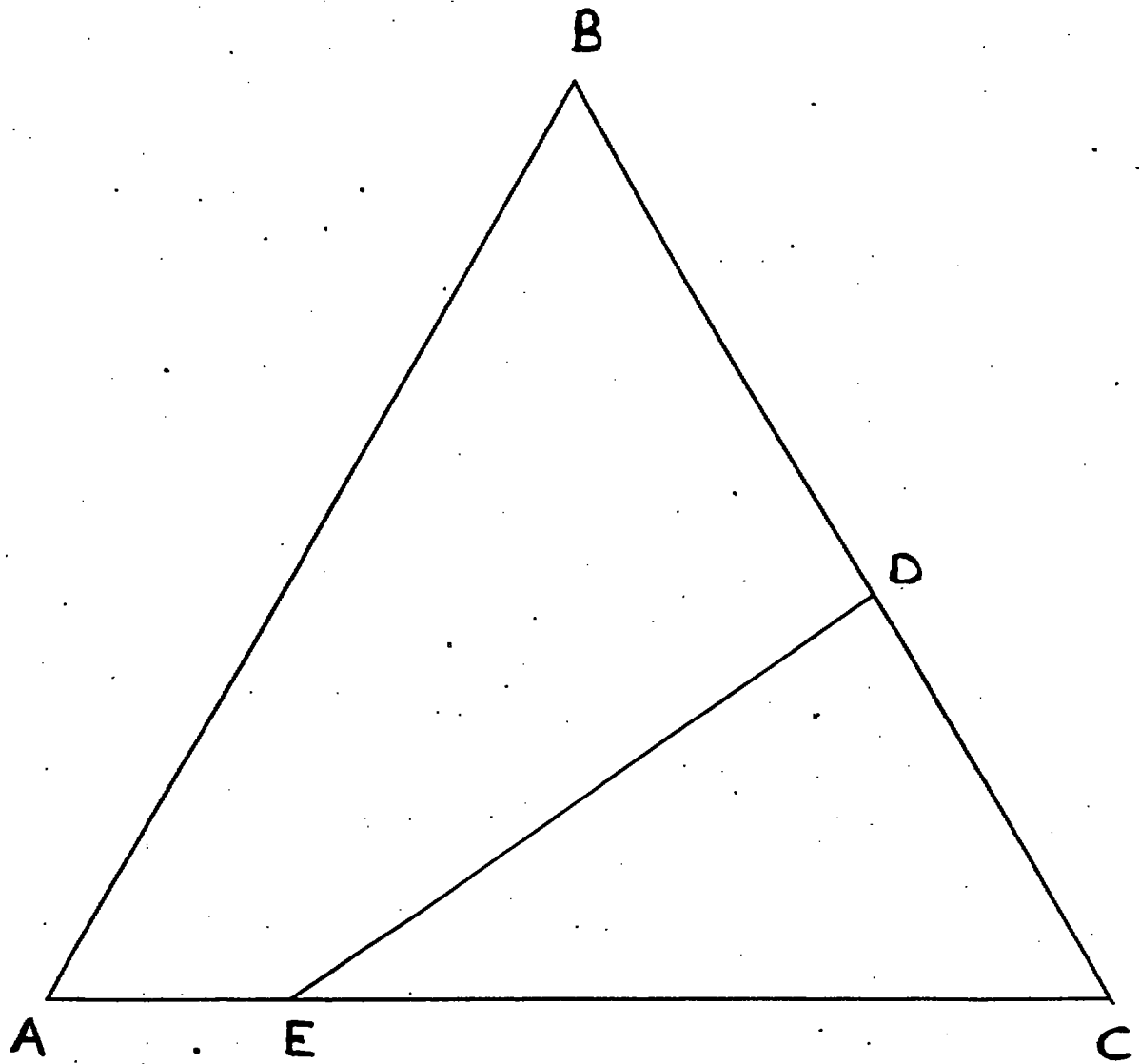
The subject of the present invention is more particularly a process for ammoxidation of alkanes in vapour phase in the presence of a solid catalyst whose active phase contains molybdenum and oxygen, characterized in that the said active phase also contains at least one element chosen from the group consisting of the alkaline-earth metals, Mn, Fe, U, La, Co, Ni, Zn, Ag, Cd, W, Zr, Pb, Te, Ga, Al, B, Nb and Ta.

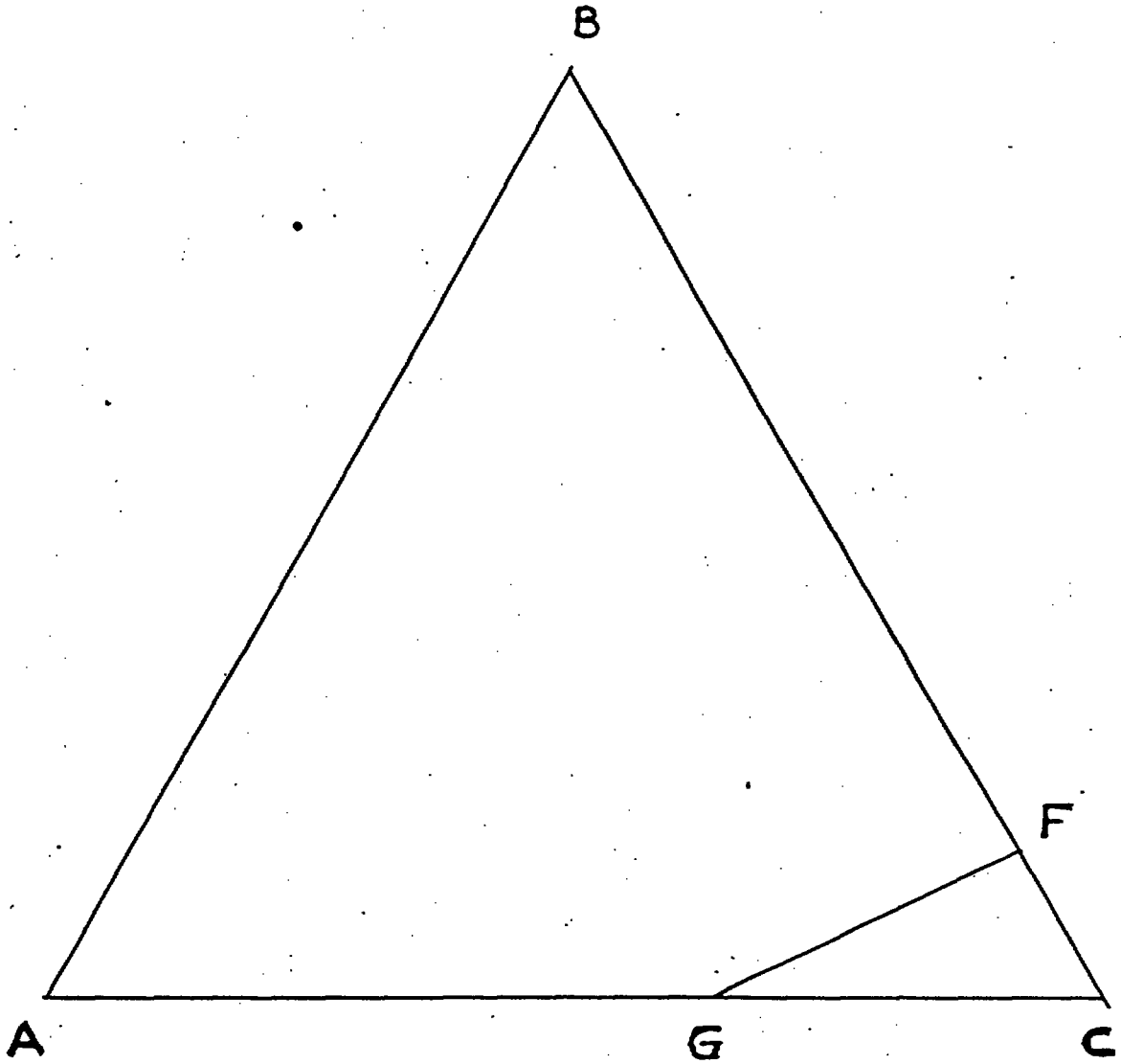
The present invention is suitable more particularly for the ammoxidation of propane to a mixture containing acrylonitrile and propylene.

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CLAIMS

REPLACEMENT SHEET 80
☐ Description : page ... to page ...
☒ Claim(s) : page 50 to page 52
☐ Drawing(s) : page ... to page ...
☒ Abstract : page 53 to page ...

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1. In a process for the ammoxidation of an alkane into an α,β -ethylenically unsaturated nitrile, by reacting an acyclic alkane having 3 or more carbon atoms per molecule with ammonia and oxygen, the improvement comprising conducting said ammoxidation in vapor phase and in the presence of a solid catalyst, said solid catalyst comprising a catalytically effective amount of an active catalytic phase, said active catalytic phase consisting essentially of a mixed oxide of molybdenum and at least one metal selected from the group consisting of Mg, Ca, Mn, Fe, U, La, and Co.
2. The process according to claim 1, wherein said at least one metal is selected from the group consisting of Mn, Fe, Co, U and La.
3. The process according to claim 1, wherein said at least one metal is selected from the group consisting of Mg, Ca, U, La, Fe and Co.
4. The process as defined by claim 1, wherein said active catalytic phase consists essentially of manganese, uranyl, cobalt or iron molybdate.
5. The process as defined by claim 1, wherein said alkane is propane.
6. The process as defined by claim 1, wherein said alkane has from 3 to 12 carbon atoms.
7. The process as defined by claim 1, carried out in the presence of water vapor.
8. The process as defined by claim 1, comprising reacting gaseous admixture of from 5% to 70% of said alkane, from 3% to 50% of ammonia, and from 3% to 45% of oxygen.
9. The process as defined by claim 8, the composition of said gaseous admixture

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being outside of the explosive region thereof.

10. The process as defined by claim 8, said gaseous admixture comprising an inert diluent therefor.

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11. The process as defined by claim 1, carried out at a temperature ranging from 350° to 550° C.

12. The process as defined by claim 1, carried out at a total pressure ranging from
10 1 to 6 bar.

13. The process as defined by claim 8, carried out an hourly space velocity of said gaseous admixture ranging from 100 to 36,000 h⁻¹.

15 14. The process as defined by claim 1, said solid catalyst further comprising an inert support substrate having said active catalytic phase deposited thereon.

15. The process as defined by claim 1, said oxygen reactant comprising air.

20 16. The process as defined by claim 5, comprising the ammoxidation of propane into acrylonitrile and propylene.

17. The process for the ammoxidation of an alkane into an α,β -ethylenically unsaturated nitrile, by reacting an acyclic alkane having at least 3 carbon atoms per
25 molecule with ammonia and oxygen, in vapor phase and in the presence of a solid catalyst, said solid catalyst comprising a catalytically effective amount of an active catalytic phase, said active catalytic phase consisting essentially of a mixed oxide of molybdenum and two metals selected from the group consisting of Mg, Ca, Mn, Fe, U, La, and Co.

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18. In a process for the ammoxidation of an alkane into an α,β -ethylenically

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unsaturated nitrile, by reacting an acyclic alkane having 3 or more carbon atoms per molecule with ammonia and oxygen, the improvement comprising conducting said ammoxidation in vapor phase and in the presence of a solid catalyst, said solid catalyst, comprising a catalytically effective amount of an active catalytic phase, said
5 active catalytic phase consisting essentially of an orthomolybdate of at least one metal selected from the group consisting of Mg, Ca, Mn, Fe, U, La, and Co.

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PROCESS FOR AMMOXIDATION OF SATURATED HYDROCARBONS

ABSTRACT

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

The subject of the present invention is more particularly a process for ammoxidation of alkanes in vapour phase in the presence of a solid catalyst whose active phase contains molybdenum and oxygen, characterized in that the said active phase also contains at least one element chosen from the group consisting of the alkaline-earth metals, Mn, Fe, U, La, Co, Ni, Zn, Ag, Cd, W, Zr, Pb, Te, Ga, Al, B, Nb and Ta.

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

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