

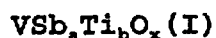
AMMOXIDATION CATALYSTS AND PROCESS FOR THEIR PREPARATION

The present invention relates to a process for preparing mixed vanadium, antimony and titanium oxides containing a crystalline phase of the rutile  $TiO_2$  type, to mixed oxides produced by such a process and to a process for the ammoxidation of alkanes using such an oxide as a catalyst.

Certain mixed vanadium and antimony oxides or mixed oxides of vanadium, antimony and other metals described, among numerous other mixed oxides, in FR-A-2 072 334.

Similarly, EP-A-0 492 805 describes the preparation of innumerable compounds, including mixed oxides of vanadium, antimony, tin and titanium, by mixing compounds of various metals in an aqueous solution of hydrogen peroxide, subsequently calcining said mixture at a temperature of greater than  $750^\circ C$ , preferably greater than  $780^\circ C$ , and then treating the calcined mixture with a monohydroxy or dihydroxy compound. All of these compounds have a Ti:V molar ratio of 0.1:1 or 0.2:1.

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



in which:

- a represents an integer or fractional number equal to or greater than 0.1,
- b represents an integer or fractional number

equal to or greater than 0.1, and

- x represents an integer or fractional number determined by the oxidation states of the other elements,

wherein:

- respective compounds of vanadium, of antimony and of titanium are dissolved in at least one saturated alcohol,

- the alcoholic solution thus obtained is contacted with water, for example in aqueous solution containing an ammonium salt, in order to precipitate the mixed oxide, and

- the mixed oxide is separated and calcined.

These mixed oxides exhibit X-ray diffraction lines which are characteristic of a crystallographic phase of the rutile  $\text{TiO}_2$  type and do not exhibit X-ray diffraction lines which are characteristic of the crystallographic phases of  $\alpha\text{-Sb}_2\text{O}_4$ , cervantite, and/or  $\text{Sb}_6\text{O}_{13}$ .

The characteristic lines of the phase of the rutile  $\text{TiO}_2$  type correspond to the following lattice spacings d (in Å):

3.24-3.27

2.48-2.52

2.29-2.31

2.18-2.21

2.05-2.07

1.68-1.70

1.62-1.64

1.48-1.51

1.45-1.50

1.42-1.46

1.36-1.37

1.30-1.31

1.24-1.26.

The characteristic lines of the  $\alpha$ - $\text{Sb}_2\text{O}_4$  (cervantite) phase correspond to the following lattice spacings  $d$  (in Å):

4.45

3.45

3.07

2.93

2.73

2.65

2.47

2.40

2.24

2.16

2.00

1.91

1.86

1.78

1.72

1.63

1.59

1.56

1.52

1.47

1.42

1.37.

The characteristic lines of the  $\text{Sb}_2\text{O}_3$  phase

correspond to the following lattice spacings  $d$  (in Å):

5.95  
3.11  
2.97  
2.58  
2.36  
2.10  
1.98  
1.82  
1.74  
1.57  
1.55  
1.48  
1.44.

Among the mixed oxides of formula (I) defined above, which are prepared by the process of the invention, preference is given to those for which:

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

Finally, more particular preference is given to the mixed oxides of formula (I) for which:

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

The vanadium, antimony and titanium compounds employed in the process must be soluble in a saturated

alcohol or a mixture of saturated alcohols. In the present text, a compound is regarded as soluble when its solubility, measured at 25°C, is at least 5 grams per litre of saturated alcohol. These compounds can be introduced together; they can also first of all be dissolved separately in an alcohol, the separate alcoholic solutions thus obtained being subsequently mixed with one another. Generally, but without limitation, an alcoholic solution is prepared by dissolving the various compounds, without intermediate preparation of solutions of each of the vanadium, antimony and titanium compounds.

Examples of soluble vanadium compounds which may be mentioned are vanadyl acetylacetonate, vanadyl trichloride, vanadium trifluoride, vanadium tetrafluoride, vanadium pentafluoride, vanadium tribromide, vanadium dichloride, vanadium trichloride, vanadium tetrachloride and vanadium triiodide.

Examples of soluble antimony compounds which may be mentioned are antimony pentachloride, antimony trichloride, antimony tribromide, antimony trifluoride, antimony triiodide, antimony trioxide and antimony hydride.

Examples of soluble titanium compounds which may be mentioned are titanium dichloride, titanium tetrachloride, titanium trichloride, titanium tribromide, titanium tetrabromide, titanium tetrafluoride and titanium diiodide.

The saturated alcohols employed in the process of the invention are, more particularly, alkanols and cycloalkanols. It is preferred to use alkanols and cycloalkanols whose boiling point is not excessively high, in order to facilitate the operations of separation or of

recycling by distillation or evaporation. Consequently, alkanols having from 1 to 6 carbon atoms, such as methanol, ethanol, n-propanol, 2-propanol, n-butanol, 2-butanol, tert-butanol, pentanols and hexanols, and cyclohexanol are preferred.

The alcoholic solution obtained above is then mixed with water, so as to precipitate the mixed oxides. The operation is preferably carried out in an aqueous solution of an ammonium salt, in particular an ammonium carboxylate (for example acetate, citrate or tartrate), ammonium oxalate, ammonium carbonate or ammonium hydrogen phosphate, which enables a pH of from 5 to 9, and preferably about 7, to be obtained. Ammonium acetate at a concentration of two mol per litre in water has a pH of about 7.

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

After precipitation of the mixed oxides of the invention, they are separated from the saturated alcohol/water liquid by any technique which is commonly used for this type of operation, especially by filtration. The isolated mixed oxides are then dried, at atmospheric pressure or under reduced pressure, at a temperature of, for example,

from 30°C to 200°C, these values being of no critical importance.

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

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

In accordance with the present invention, alkanes preferably having from 3 to 12 carbon atoms per molecule are reacted in the vapour phase with ammonia and oxygen.

Within the context of the present process it is of course possible to use diluent gases which are inert under the reaction conditions, such as helium, nitrogen and argon. Likewise, steam can be added to the gaseous reaction mixture within wide limits. The reactive gas (alkane, ammonia, oxygen) can thus be diluted with an inert diluent and/or with steam. In this context, the content of steam can vary within wide limits, in particular from 0 to 50 vol% and, preferably, from 3 to 30 vol%. For good implementation of the process according to the invention, the content of reactive gas will be at least 3 vol% and preferably at least 20 vol%.

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

The content of alkane in the reactive gas is

preferably from 5 to 70 vol%. That of ammonia is preferably from 3 to 50 vol%, and that of oxygen is preferably from 3 to 45 vol%.

For good implementation of the process according to the invention, the composition of the reactive mixture will preferably be chosen so as to be outside the explosive region.

Starting from propane, the mixture obtained will essentially contain propylene and acrylonitrile. Acrylonitrile is an intermediate which is produced industrially on a large scale, while propylene is a raw material which is traditionally used to produce acrylonitrile and various other intermediate products which are well known to the person skilled in the art.

Starting from isobutane, the mixture obtained will comprise methacrylonitrile and isobutene or n-butenes.

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

If the alkane employed is of technical grade, it will not contain significant quantities of compounds having ethylenic unsaturation. Thus, the propane employed will generally contain only minor amounts of propylene, for example less than 10 vol%.

The process according to the invention is carried out in the form of a vapour phase reaction. Consequently, any device suitable for carrying out an ammoxidation or oxidation reaction in the vapour phase can be used. The process can be carried out continuously or batchwise and it can use a fixed bed or a fluidized bed.

The reaction temperature is in general from 300°C to 550°C, and preferably from 400°C to 500°C.

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

The gas flow rate is set such that the hourly volume rate is generally from 100 to 36,000 h<sup>-1</sup>, and preferably from 200 to 20,000 h<sup>-1</sup>.

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

The person skilled in the art will of course be able to find a suitable compromise between the temperature, the gas flow rate, the precise nature of the catalyst employed and the various other parameters of the reaction, taking into account his or her production objectives.

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

The catalytic phase, consisting of the active phase alone or of the active phase deposited on an inorganic oxide or mixed with the said inorganic oxide, can then be employed

in bulk form or in the particulate state; it can therefore be used in powder form or can be shaped, for example as balls, pellets, extrudates or crushed particles, according to various known techniques.

For implementation of the process in a fixed bed, examples of possible such techniques are pelletizing or coating onto an inert substrate or onto a ceramic or metal substrate of monolithic type.

For implementation of the process in a moving bed or in a fluidized bed, the catalytic phase is generally shaped by atomizing, drying and calcining.

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

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

The catalytic phases can also be deposited on an inert substrate or can be coated. The nature of this substrate is not critical, provided that it is chemically inert with regard to the reactants under the chosen reaction conditions. Examples which may be mentioned of substrates suitable for the preparation of catalysts which can be used in the context of the process according to the invention are:

silica, alumina, silica-alumina, sintered clay, carborandum, magnesia, magnesium silicate and diatomaceous earth. This substrate is preferably nonporous and can in particular be based on a refractory oxide in the particulate form, the most commonly employed substrate being clay-based. This substrate can, for example, consist of inert, complete, solid and rough clay balls with a diameter of between 0.5 and 6 mm.

The precise diameter of the balls will be chosen according to the pressure drop which is acceptable in the reactor. This substrate can also be made nonporous by enamelling.

This substrate can also be a ceramic substrate, the said substrate preferably being in the form of an inert and rigid structure of a monolithic type comprising channels or ducts. Supports of this kind are well known and have been widely described in the literature. The substrates used which are made from ceramic materials are, in particular, those comprising cordierite, alumina, mullite, porcelain or the carbides of boron or of silicon as the principal material.

This substrate may also be a metal substrate. Such substrates are well known. Suitable metal substrates are, in particular, those obtained from alloys of iron, nickel and chromium, or those obtained from alloys of iron, chromium, aluminium and cobalt, such as those known under the tradename KANTHAL, or those obtained from alloys of iron, chromium, aluminium and yttrium, which are known under the tradename FECRALLOY. The metal may also be carbon steel or simple cast iron.

When a coated catalyst is employed, the quantity of

catalytic phase can vary within wide limits and in practice is from 1 to 50 %, and preferably from 5 to 35 %, by weight relative to the overall combination of substrate + catalytic phase.

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

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

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

The products of the reaction can be recovered from

the effluent gases by any appropriate means. For example, the effluent gases can pass into a condenser containing dilute sulphuric acid in order to neutralize the unreacted ammonia. The gases can then pass through a refrigerated absorbing column in order to condense the acrylonitrile, acetonitrile and hydrocyanic acid, the uncondensed vapours containing mainly unreacted propane, propylene, light hydrocarbons and, if appropriate, CO<sub>2</sub>. The acrylonitrile and hydrocyanic acid can then be separated from the acetonitrile by distillation, and the acrylonitrile/hydrocyanic acid mixture recovered can then in turn be distilled in order to separate the acrylonitrile from the hydrocyanic acid.

The Examples below further illustrate the present invention.

#### EXAMPLES OF THE PREPARATION OF MIXED OXIDES

EXAMPLE 1 - Preparation of the mixed oxide (A) according to the invention, of the following empirical formula: VSb<sub>5</sub>Ti<sub>5</sub>O<sub>x</sub>

A solution of 10.92 g of anhydrous TiCl<sub>4</sub>, 3.05 g of vanadyl acetylacetonate and 17.22 g of SbCl<sub>5</sub> in 100 ml of absolute ethanol is prepared.

The ethanolic solution is poured dropwise into 500 ml of an aqueous solution containing ammonium acetate (2 mol/litre) to give an initial pH of the order of 7.0. During precipitation of the mixed V, Sb and Ti oxides, the pH, which tends to decrease owing to the liberation of hydrochloric acid, is kept constant by adding concentrated aqueous ammonia solution (30 % strength by weight).

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

The compound of formula  $\text{VSb}_5\text{Ti}_5\text{O}_x$  thus obtained is subsequently compressed under a pressure of 4300 bars. Pellets with a diameter of 3 cm and a thickness of approximately 0.5 cm are then obtained. These pellets are crushed into fragments with a particle size of from 0.3 to 0.8 cm, constituting the catalyst (A) according to the invention.

EXAMPLES 2 AND 3 - Preparation of various mixed oxides according to the invention

Various mixed oxides are prepared by the procedure described in Example 1 but using different quantities of vanadyl acetylacetonate (Example 3) or antimony pentachloride (Example 2).

Mixed oxides according to the invention are thus obtained, having the following formulae:

Example 2       $\text{VSb}_{10}\text{Ti}_5\text{O}_x$  (reference D)

Example 3       $\text{VSb}_{10}\text{Ti}_{10}\text{O}_x$  (reference E)

COMPARATIVE TEST 1 - Preparation of the mixed oxide (B) prepared according to a process of the prior art, of the following empirical formula:  $\text{VSb}_5\text{Ti}_5\text{O}_x$

The mixed oxide of composition  $\text{VSb}_5\text{Ti}_5\text{O}_x$  is prepared in 3 stages by coprecipitation in an aqueous medium.

9.52 g of titanium tetrachloride are dissolved in 100 ml of an  $\text{HCl}/\text{H}_2\text{O}$  solution with a pH of 0.5-1.0. The solution is held at a low temperature by means of an ice/water bath. It

is then heated to 90°C, and this temperature is held for 1 hour.

In a second solution similar to that above, 2.65 g of vanadyl acetylacetonate and 15.0 g of antimony pentachloride are dissolved. This solution is then poured into a buffer solution of ammonium acetate whose pH is kept constant at approximately 7 by addition of aqueous ammonia.

The two solutions thus prepared are mixed and are left with stirring for 30 minutes. The mixed oxide which precipitates is separated off by centrifugation, washed, dried at 140°C for 12 hours and then calcined for 3 hours at 700°C.

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

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

The mixed oxide of composition  $\text{VSb}_5\text{Ti}_5\text{O}_x$  is prepared by the procedure described in Example M of US-A-5,008,427.

The compound of formula  $\text{VSb}_5\text{Ti}_5\text{O}_x$  thus obtained is then compressed under a pressure of 4300 bars. Pellets with a diameter of 3 cm and a thickness of approximately 0.5 cm are then obtained. These pellets are crushed into fragments with a particle size of from 0.3 to 0.8 cm, constituting the

catalyst (J) not according to the invention.

EXAMPLES 4 TO 6 - Preparation of various mixed oxides according to the invention

Various mixed oxides are prepared by the procedure described in Example 1 but using different quantities of vanadyl acetylacetonate, titanium tetrachloride or antimony pentachloride.

Mixed oxides according to the invention are thus obtained, having the following formulae:

Example 4       $\text{VSbTi}_{6.75}\text{O}_x$  (reference F)

Example 5       $\text{VSb}_{1.5}\text{Ti}_{0.2}\text{O}_x$  (reference H)

Example 6       $\text{VSb}_{1.5}\text{Ti}_1\text{O}_x$  (reference I)

CHARACTERIZATION OF THE MIXED OXIDES PREPARED

The various mixed oxides A, D, E, F, H and I according to the invention and B not according to the invention were characterized by X-ray diffraction on a PHILIPS P1800 diffractometer in the measurement range of  $10^\circ$  to  $70^\circ$  in  $2\theta$ . The characteristic lines of the various oxides were then compared with the characteristic lines of the pure products, reported in International Tables of X-Ray crystallography.

The diffraction patterns obtained demonstrate clearly that the catalysts (A), (D) and (E) are composed of a rutile phase whose unit cell parameters are very similar to those of rutile  $\text{TiO}_2$ . The diffraction pattern for the oxide (B) of the prior art shows that the oxide (B) is composed of a rutile  $\text{TiO}_2$  phase and of the oxide  $\text{Sb}_2\text{O}_3$ .

GENERAL PROCEDURE FOR THE AMMOXIDATION TESTS

The catalyst sample is brought initially on a measuring bench to a temperature of  $150^\circ\text{C}$  while being purged with

helium for 10 min, and is then subjected to a gas flow whose composition is specified for each Example and which comprises propane, ammonia, oxygen, helium and, if appropriate, steam.

The total pressure of the reaction mixture is from 1 to 6 bars and is likewise specified for each Example.

The total gas flow rate is such that the hourly volume rate (HVR) is from 100 to 36,000 h<sup>-1</sup>, the precise value of which is indicated for each Example.

Volume of active phase: 25 cm<sup>3</sup>.

The principle of the ammoxidation test for propane is as follows:

- The catalyst is brought to a temperature T<sub>1</sub>, for example 310°C, and, after stabilization for 30 min at the temperature T<sub>1</sub>, the composition of the mixture at the reactor outlet is determined by gas chromatography.
- The percentage conversions and the selectivities obtained with the catalyst examined at the inlet temperature T<sub>1</sub> are calculated by relationships of the type:  
  
conversion of propane (mol %) = propane converted/  
propane introduced  
  
selectivity for acrylonitrile (mol %) = propane converted  
to acrylonitrile/propane converted.
- The catalyst is then brought from 310 to 550°C in 20°C steps, and the percentage conversions and selectivities are determined every 40 min.

In the ammoxidation Examples below, the following conventions are utilized:

temp. = reaction temperature

DC(C<sub>3</sub>H<sub>8</sub>) = conversion of propane

S(ACN) = selectivity for acrylonitrile

S(ACN+C<sub>3</sub>H<sub>6</sub>) = selectivity for acrylonitrile and propylene

S(ammox) = selectivity for acetonitrile, hydrocyanic acid and other ammoxidation by-products

prod. ACN = productivity in terms of acrylonitrile, expressed in g of acrylonitrile formed/litre of catalyst x hour.

The balance to 100 % of the selectivities corresponds to the formation of CO and CO<sub>2</sub> and, where appropriate, of methane, ethane and ethylene.

#### EXAMPLES OF THE AMMOXIDATION OF PROPANE

##### EXAMPLES 7 TO 12 AND COMPARATIVE TESTS 3 AND 4

Ammoxidation of propane is carried out as described above using, as catalysts, the active phases consisting of the mixed oxides A, D, E, F, H and I of the invention, and the mixed oxides B and J not according to the invention.

The specific conditions employed are as follows:

- hourly volume rate = 1700 h<sup>-1</sup>
- total pressure = 1.3 bars
- composition by volume of the reaction mixture:

C<sub>3</sub>H<sub>8</sub> = 25 %

NH<sub>3</sub> = 10 %

O<sub>2</sub> = 20 %

He = 45 %

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

| Examples           | Catalyst used | Temp (°C) | DC (C <sub>2</sub> H <sub>2</sub> ) (in %) | S (ACN) (in %) | S (ACN + C <sub>2</sub> H <sub>2</sub> ) (in %) | S (am-mox) (in %) | prod. ACN (g/l x h) |
|--------------------|---------------|-----------|--------------------------------------------|----------------|-------------------------------------------------|-------------------|---------------------|
| Example 7          | A             | 388       | 6                                          | 25             | 31                                              | 42                | 15                  |
|                    |               | 408       | 11                                         | 34             | 39                                              | 28                | 37                  |
|                    |               | 428       | 22                                         | 36             | 39                                              | 14                | 79                  |
|                    |               | 447       | 24                                         | 43             | 46                                              | 15                | 102                 |
| Example 8          | D             | 404       | 12                                         | 40             | 48                                              | 23                | 48                  |
|                    |               | 422       | 14                                         | 46             | 51                                              | 21                | 71                  |
|                    |               | 442       | 16                                         | 53             | 56                                              | 16                | 83                  |
|                    |               | 461       | 18                                         | 53             | 57                                              | 15                | 95                  |
| Example 9          | E             | 407       | 13                                         | 32             | 38                                              | 25                | 41                  |
|                    |               | 426       | 19                                         | 39             | 43                                              | 21                | 74                  |
|                    |               | 445       | 19                                         | 49             | 52                                              | 14                | 92                  |
|                    |               | 465       | 19                                         | 51             | 54                                              | 14                | 96                  |
| Example 10         | F             | 407       | 8                                          | 21             | 48                                              | 33                | 17                  |
|                    |               | 427       | 13                                         | 25             | 40                                              | 36                | 32                  |
|                    |               | 447       | 17                                         | 31             | 42                                              | 23                | 52                  |
|                    |               | 468       | 21                                         | 36             | 43                                              | 18                | 75                  |
| Example 11         | H             | 389       | 10                                         | 29             | 46                                              | 25                | 29                  |
|                    |               | 407       | 14                                         | 32             | 46                                              | 23                | 44                  |
|                    |               | 428       | 21                                         | 35             | 47                                              | 18                | 73                  |
|                    |               | 446       | 24                                         | 37             | 50                                              | 17                | 88                  |
| Example 12         | I             | 388       | 15                                         | 20             | 35                                              | 30                | 30                  |
|                    |               | 408       | 20                                         | 35             | 45                                              | 29                | 69                  |
|                    |               | 425       | 24                                         | 37             | 44                                              | 12                | 88                  |
|                    |               | 446       | 25                                         | 39             | 48                                              | 7                 | 97                  |
| Comparative test 3 | B             | 424       | 5                                          | 60             | 83                                              | 8                 | 30                  |
|                    |               | 443       | 7                                          | 58             | 77                                              | 8                 | 40                  |
|                    |               | 464       | 9                                          | 49             | 72                                              | 6                 | 44                  |
|                    |               | 485       | 16                                         | 35             | 57                                              | 5                 | 52                  |

| Examples           | Catalyst used | Temp (°C) | DC (C <sub>3</sub> H <sub>8</sub> ) (in %) | S (ACN) (in %) | S (ACN + C <sub>3</sub> H <sub>8</sub> ) (in %) | S (am-mox) (in %) | prod. ACN (g/l × h) |
|--------------------|---------------|-----------|--------------------------------------------|----------------|-------------------------------------------------|-------------------|---------------------|
| Comparative test 4 | J             | 426       | 2                                          | 22             | 57                                              | 22                | 4                   |
|                    |               | 448       | 3                                          | 32             | 63                                              | 21                | 9                   |
|                    |               | 468       | 4                                          | 42             | 67                                              | 16                | 17                  |

Table 1



CLAIMS

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



in which:

- a represents an integer or fractional number equal to or greater than 0.1,
- b represents an integer or fractional number equal to or greater than 0.1, and
- x represents an integer or fractional number determined by the oxidation states of the other elements,

wherein:

- respective compounds of vanadium, of antimony and of titanium are dissolved in at least one saturated alcohol,
- the alcoholic solution thus obtained is contacted with water in order to precipitate the mixed oxide, and
- the mixed oxide is separated and calcined.

2. Process according to claim 1, in which:

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

3. Process according to claim 2, in which:

- a represents an integer or fractional number of from 0.5 to 50, and



- b represents an integer or fractional number of from 1 to 40.

4. Process according to any one of claims 1 to 3, in which the soluble vanadium compound is vanadyl acetylacetonate, vanadyl trichloride, vanadium trifluoride, vanadium tetrafluoride, vanadium pentafluoride, vanadium tribromide, vanadium dichloride, vanadium trichloride, vanadium tetrachloride or vanadium triiodide.

5. Process according to any one of claims 1 to 4, in which the soluble antimony compound is antimony pentachloride, antimony trichloride, antimony tribromide, antimony trifluoride, antimony triiodide, antimony trioxide or antimony hydride.

6. Process according to any one of claims 1 to 5, in which the soluble titanium compound is titanium dichloride, titanium tetrachloride, titanium trichloride, titanium tribromide, titanium tetrabromide, titanium tetrafluoride or titanium diiodide.

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

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

9. Process according to any one of claims 1 to 8, in which the alcoholic solution obtained is subsequently mixed with an aqueous solution of an ammonium salt which enables a pH of from 5 to 9 to be obtained in order to precipitate the mixed oxide.

10. Process according to claim 9, in which the ammonium



salt is ammonium carboxylate, ammonium oxalate, ammonium carbonate or ammonium hydrogen phosphate.

11. Process according to claim 9 or 10, in which the pH is about 7.

12. Process according to any one of claims 1 to 11, in which the pH of the mixed solution is maintained at about 7 by progressively neutralizing the acidity which is formed during the precipitation of the mixed oxides by means of a basic compound.

13. Process according to claim 12, in which the acidity is neutralized by controlled, progressive addition of aqueous ammonia.

14. Process according to any one of claims 1 to 13, in which the separated mixed oxides are calcined at a temperature of from 400°C to 800°C.

15. Process according to claim 14, in which the mixed oxides are calcined at a temperature of from 500°C to 750°C.

16. Process for the ammoxidation of alkanes in the vapour phase in the presence of a solid catalyst containing at least one active phase which comprises at least one mixed oxide of empirical formula (I) and which has been prepared by a process as defined in any one of claims 1 to 15.

17. Process according to claim 16, in which at least one alkane having from 3 to 12 carbon atoms per molecule is reacted in the vapour phase with ammonia and oxygen.

18. Process according to claim 17, in which the alkane is propane or isobutane.

19. Process according to any one of claims 16 to 18, in which, within the reactive gas composed of the alkane, ammonia



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and oxygen, the alkane content is from 5 to 70 vol%, the ammonia content is from 3 to 50 vol% and the oxygen content is from 3 to 45 vol%.

20. Process according to any one of claims 16 to 19 in which the reaction temperature is from 300°C to 550°C.

21. Process according to claim 20 in which the reaction temperature is from 400°C to 500°C.

22. A mixed oxide of formula (I) as defined in claim 1 which has been prepared by a process as defined in any one of claims 1 to 15.