

HETEROPOLYACID-BASED CATALYSTS AND USE THEREOF
FOR THE PREPARATION OF ALIPHATIC CARBOXYLIC ACIDS

The present invention relates to a process for the preparation of carboxylic acids by controlled oxidation of the corresponding alkanes, in the presence of a catalyst whose active phase is obtainable from a heteropolyacid.

The present invention moreover relates to a composition obtained from a heteropolyacid and titanium dioxide, as support, as well as to a catalyst comprising the said composition as active phase.

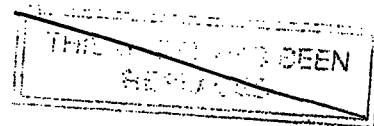
By convention, the term heteropolyacid (or HPA) will be used in this text to denote both heteropolyacids and polyoxometallates.

The production of carboxylic acids, in particular acetic acid, by controlled oxidation of the alkane, such as ethane, is a process in full development since it has the advantage of using a starting material which is of very competitive cost compared with those used in existing technologies.

Among the known processes of this type, there may be mentioned those using, besides ethane and oxygen, catalysts based, at least, on the vanadium, phosphorus and rhenium oxides. The selectivities towards acetic acid are of the order of 30 % but they remain, however, lower than those of the ethylene coproduced. In addition, this process requires the introduction into the reactor of large amounts of water and of an inert gas such as helium or nitrogen.

Another process consists in reacting the ethane and oxygen in the presence of catalysts based on at least a mixture of the molybdenum, vanadium, niobium and antimony oxides, or alternatively based on the molybdenum, vanadium, rhenium, antimony, niobium and calcium oxides. The selectivity towards acetic acid by the use of such catalysts is enhanced relative to that obtained according to the above process. However, the reaction conditions are demanding. Indeed, it is necessary to carry out the oxidation under conditions combining an elevated temperature, that is to say of the order of 300 to 400°C, and a high pressure, of the





order of 20 to 30 bar. Moreover, the processes for the preparation of such catalytic formulae are not easy to carry out.

It is known, moreover, to use catalysts whose active phase comprises oxides of vanadium, the latter being in the (IV) oxidation state, of titanium and/or of phosphorus. In the case of these catalysts, the performances are of interest in terms of selectivity towards acetic acid. However, the feed flow comprises more than 90% of diluent gas, which results in a very low productivity.

It may hence be observed that, at the present time, no process is available for the preparation of an aliphatic carboxylic acid, and more particularly acetic acid, by oxidation of an alkane which may be developed on the industrial scale and which uses catalysts that are readily manufactured.

Now, it has been found, entirely unexpectedly, that the use of catalysts whose active phase has been obtained from a heteropolyacid of formula (I), which will be defined below, in the abovementioned reaction, made it possible to overcome the abovementioned drawbacks.

Thus, the process according to the invention combines an enhanced selectivity towards carboxylic acid formed with quite unrestrictive implementation conditions, making it possible to envisage an exploitation of the reaction on the industrial scale.

In addition, the process according to the invention may be carried out with a large amount of alkane. This represents a definite advantage relative to the processes employing reaction mixtures comprising large amounts of inert diluent gas. The reason for this is that the alkane, which is only partially converted, may very readily be recycled in the reaction.

Moreover, the process according to the invention is carried out at a lower temperature than those usually employed. Now, it is entirely surprising to be able to activate alkanes, and most particularly ethane, at temperatures which may be as low as 150°C - 250°C, given the lower reactivity of ethane relative to longer-chain saturated

hydrocarbons or alternatively given the reactivity of saturated hydrocarbons relative to unsaturated hydrocarbons, which may or may not be aromatic.

Thus, the process according to the invention comprises the preparation of aliphatic carboxylic acids by controlled oxidation of the corresponding alkanes, with a source of oxygen, in the presence of a catalyst whose active phase is obtained from a heteropolyacid of formula (I):

$[A_xB_y]_f[C_zD_dE_eO_x]^{f-}$ in which:

- A represents at least one monovalent cation chosen from hydrogen, an alkali metal or the ammonium ion;
- B represents VO^{2+} , VO^{3+} , an alkaline-earth metal ion or an ion of a metal of groups VII A, VIII, I B, IV B and V B of the Periodic Table of the Elements;
- C represents W and/or Mo;
- D represents phosphorus, arsenic, antimony, silicon, germanium or boron;
- E represents vanadium and optionally at least one metal element chosen from groups V A, VII A and VIII or chromium;
- $f = a + \alpha b$; with α depending on the charge of the ion B, which is equal to 2, 3 or 4;
- c is from 5 to 20-e inclusive;
- d is from 1 to 5 inclusive; and
- e is from 1 to 9 inclusive.

Here and for all of the description, the comments relating to the Periodic Table of the Elements refer to the table published in the supplement to the bulletin of the French Chemical Society (No. 1 - January 1966).

The subject of the invention is similarly a composition comprising a titanium dioxide as support and a catalyst whose active phase is obtained from a heteropolyacid of formula (I) $[A_xB_y]_f[C_zD_dE_eO_x]^{f-}$ in which A, B, C, D, E, a, b, c, d, e and f have the same meanings as those given above.

Another subject of the invention consists of a catalyst which comprises, as active phase, the abovementioned composition.

A further subject of the present invention is the use of a catalyst as defined above in the preparation of



aliphatic carboxylic acids by controlled oxidation of the corresponding alkanes with a source of oxygen.

An additional subject of the present invention is an aliphatic carboxylic acid whenever prepared by a process as defined above.

In the text which follows, the terms titanium dioxide and titanium oxide have the same meaning.

More particularly, the element B is chosen from VO^{2+} , VO^{3+} , Cu^{2+} , Fe^{3+} , Co^{2+} , Ag^+ , Ni^{2+} , Mn^{2+} , Mg^{2+} , Bi^{3+} , Sn^{2+} and Sn^{4+} ions.

The element B is preferably chosen from the VO^{2+} and VO^{3+} ions.

As regards the element E which is other than vanadium, this is more particularly chosen from chromium, manganese, iron, cobalt and nickel.

According to a preferred variant of the invention, the heteropolyacid entering into the preparation of the active phase corresponds to the formula (I) in which D is phosphorus, E is vanadium, d is 1, c is from 1 to 3 and the sum $c + e$ is 12.

According to a particular embodiment, the catalyst employed has an active phase which also comprises a support.

By way of support suitable for implementing this particular embodiment, there may, for example, be mentioned the titanium, silicon, zirconium, cerium and tin dioxides, alumina and silica-alumina, it being possible for these compounds to be used alone or as a mixture.

The support is preferably chosen from titanium dioxide and zirconium dioxide, the former being preferred.

According to a variant of this embodiment, the active phase of the catalyst has an atomic proportion $(C + E)/\text{metal element}$ of the support of from 0.1 to 30 %. The term metal element of the support refers to the titanium, zirconium, cerium, etc.

The abovementioned atomic ratio is preferably from 5 to 20%.

In the case where the active phase comprises a support, the distribution between the two constituents of the active phase is such that the heteropolyacid of formula (I)



is more particularly dispersed at the surface of said support.

According to a first embodiment, the catalyst is employed in bulk form, that is to say that it is a catalyst comprising only the active phase obtained from the heteropolyacid and, where appropriate, from the support.

According to a second embodiment, the catalyst is employed in dilute form, that is to say that the abovementioned active phase is mixed with an inert material.

In this latter case, the active phase may be either deposited on the inert material or coated on or alternatively may be mixed therewith.

By way of materials which may be used as inert materials, there may be mentioned: sintered clay, magnesia, magnesium silicate and diatomaceous earth. These types of inert material may be used in porous or non-porous form. The inert material used is preferably in non-porous form. If necessary, an enamelling may be carried out in order to render it thus.

The ceramic materials, for example of the cordierite, mullite, porcelain, silicon nitride, boron nitride and silicon carbide type, may also be used as an inert material.

The catalyst used in the process according to the invention, which may or may not be diluted, is, for example, in the form of particles or in monolith form.

If the catalyst consists of particles, the size of these particles depends on the mode of use of the catalyst. It may thus vary within a wide range, such as especially to be between a few micrometres and about ten millimetres. More particularly, and as a guide, a catalyst used in a fixed bed has a particle size distribution generally from 0.5 to 6 mm. The particle size of a catalyst used in a fluidized or moving bed is usually from 5 to 700 microns, and preferably from 5 to 200 microns, for 80 % of the particles.

If the catalyst consists of particles, all forms are suitable for carrying out the invention. Thus, the catalyst may, for example, be in the form of beads or rings. The term rings denotes hollow objects of, for example, circular,

parallelepipedal and ellipsoid cross-section. Any other type of complex structure, for example obtained by extrusion of the inert material (for example in the form of a cross or star) may likewise be envisaged.

In a standard manner, the amount of inert material entering into the composition of the catalyst varies within a wide range, depending most often on the mode of formation of the catalyst.

Thus, catalysts obtained by coating or depositing the active phase onto the inert material have an amount of active phase which is usually from 0.1 to 30%, and preferably from 2 to 20%, of the total weight of catalyst (active phase + inert material).

In the cases where the catalyst comprises the active phase dispersed in an inert material, the amount of active phase is generally from 1 to 90% of the total weight of catalyst.

According to a preferred embodiment of the invention, the active phase of the catalyst coats the inert material present.

The catalyst may be prepared according to any standard, simple and reproducible method, which constitutes an additional advantage of the invention.

The heteropolyacids are known compounds and a person skilled in the art may refer to publications concerning them in order to prepare them.

As more particularly regards the heteropolyacids, for which A represents a hydrogen atom, it is especially possible to use two types of process.

According to a first method, which is more particularly suitable for the preparation of heteropolyacids in which b is equal to 0 and d is equal to 1, a mixture comprising the constituent elements of the heteropolyacid, preferably in oxide form, is maintained at reflux in water for 24 hours.

Another method for producing heteropolyacids of the same type as above and for which the value of c is from 6 to 12 consists in preparing a solution of the constituent elements of the HPA, which are present in the form of alkali

metal or alkaline-earth metal salts. This solution is obtained by dissolving said compounds in water.

Once the solution is obtained, it is neutralized by the addition of an inorganic acid such as hydrochloric acid in particular. The resulting product is extracted from the medium with ether and then placed in contact with distilled water to give an aqueous solution, from which the heteropolyacid may be crystallized.

On conclusion of each of these two methods, it is possible to obtain the desired heteropolyacid by evaporation or crystallization. This product may be used directly as a catalyst in the reaction according to the invention, optionally after having undergone a calcination step which will be described below.

In a usual manner and in the case where the catalyst used comprises a support, the placing in contact of the heteropolyacid with the said support is carried out by means of, for example, a dry impregnation, although other routes are not excluded in principle. In this respect, there may be mentioned the mixing of the various constituents, heteropolyacid and support, in solid form for example.

According to the impregnation method, the support as defined previously is placed in contact with a solution of heteropolyacid in an amount such that the atomic proportion, $(C + E)/\text{metal element of the support}$, is generally from 0.1 to 30% and preferably from 5 to 20%.

The resulting suspension is then dried. This drying step may advantageously be carried out in two stages: the first stage consisting in evaporating off the solvent or dispersion medium of the mixture, more particularly the water, to dryness. The second stage consisting in drying the paste thus obtained.

Generally, the first step is performed at a temperature of from 20 to 100°C under vacuum or otherwise, for the time necessary to obtain a paste.

The evaporation is usually carried out with stirring.

The paste obtained is then dried, in a second stage, under an atmosphere which is preferably non-reducing, such as

under oxygen or air, for example for an average duration of 15 hours.

The drying temperature is usually from 100 to 150°C.

It should be noted that other drying methods may be envisaged for example, drying of the suspension by spraying in any type of apparatus and under conditions known to those skilled in the art.

The dried product may then be subjected to a calcination step.

This step is performed, in a standard manner, under a non-reducing atmosphere. Air is advantageously used, but oxygen may be employed equally well.

The calcination temperature is usually from 200 to 500°C.

The duration of the operation is generally from 1 to 24 hours.

Prior to and/or subsequent to the calcination step, the dried product may undergo a deagglomeration step.

In the case where the catalyst used in the process according to the invention comprises an inert material, the coating method is preferably used.

Thus, the inert material, preferably in the form of coarse particles, and the active phase are placed together in a high shear mixer (LODIGE-type machines) or in a granulation machine (granulators, in drum or plate form).

The operation is generally carried out at a temperature of from 20 to 150°C for the time necessary to coat the inert material with the desired amount of active phase, more particularly under air, for at least 30 minutes.

The particles thus obtained are usually calcined at a temperature from 300 to 500°C.

The duration of the calcination is generally at least 3 hours.

Obviously, all these modes of preparation of the heteropolyacid, and of placing the said HPA in contact with the support and/or the inert material, are given merely as a guide and can in no case constitute an exhaustive list.

As has been mentioned previously, the process according to the invention consists in carrying out a

controlled oxidation of the alkane with a source of oxygen, in the presence of a catalyst as described above.

There are no specific conditions regarding the quality of the alkane used. However, for obvious reasons of separation of the acid formed, it is preferred to use ethane having a purity of at least 90%.

The reaction for the controlled oxidation of the alkane is carried out in the presence of a source of oxygen. This source may be based on pure oxygen or oxygen diluted in an inert gas, or alternatively may be based on nitrous oxide.

It is thus possible, in an advantageous manner, to carry out the oxidation reaction using air as the source of oxygen.

According to a specific embodiment of the present invention, the molar ratio between the alkane and the oxygen is less than 20%. More particularly, this ratio is from 0.01:1 to 0.2:1 or from 0.6:1 to 18:1.

According to a preferred embodiment of the invention, said ratio is from 0.6:1 to 18:1.

The oxidation reaction may also be carried out in the presence of a diluent.

The term diluent refers to water, inert gases such as nitrogen or rare gases such as helium or argon, for example. It should be noted that the diluent gases may also be gases recycled from the reaction such as carbon oxides. The diluent gas may be a combination of some or all the above mentioned gases.

The composition of the gaseous mixture, i.e. of the alkane, the source of oxygen and, where appropriate, the diluent gas, may vary within a wide range.

Except where otherwise mentioned, all the percentages given below are expressed as a molar per cent of the gaseous mixture.

In general, the alkane content in the gaseous mixture is from 0.1 to 99.9%.

According to a specific embodiment of the invention, the composition of the gaseous mixture is such that it is outside the explosive range of said mixture.

More particularly, and in order to have a gaseous

mixture whose composition is suitably outside the explosive range, said alkane content is from 0.1 to 3% or from 10 to 99%.

The alkane content in the abovementioned gaseous mixture is preferably from 10 to 99%.

The oxygen content in the gaseous mixture used likewise varies within a wide concentration range. It is generally from 0.1 to 99.9%.

According to a more specific embodiment, the oxygen content in the gaseous mixture varies from 1 and 90 % or between 97 and 99.9%.

The oxygen content of said mixture is preferably from 1 to 90%.

According to a specific variant of the invention, the reaction is carried out in the presence of water. In this case, the water content in the gaseous mixture is more particularly from 0 to 70%.

According to a specific embodiment, the water content in the abovementioned mixture is from 0 to 20%.

The inert gas content in the mixture, nitrogen being preferred, is usually from 0 to 70%.

More particularly, the mixture comprises from 0 to 20% of diluent gas.

The gaseous mixture is thus placed in contact with the catalyst according to the invention.

It should be noted that the placing in contact of the gaseous mixture with the catalyst may take place by pre-mixing all the constituents of the said mixture beforehand, or alternatively by introducing them separately. It is likewise possible to envisage a multi-stage injection of the alkane or, preferably, of the source of oxygen into the reactor.

The last two methods mentioned may preferably be adopted in the case of industrial exploitations, for reasons of safety of the process. Indeed, in this manner, the need to remove too large an amount of calories due to the exothermic nature of the reaction is avoided, and the risks of falling within the explosive range of the mixture are reduced.

The device in which the process according to the

reactions in the gas phase; the latter devices may be used continuously or discontinuously.

Thus, the reaction may be carried out in a reactor in which the catalyst is in a fixed, fluidized or transported bed, in alternative fixed beds or alternatively in a reverse-flow reactor. The process according to the invention is preferably carried out in fixed, fluidized or alternatively transported bed reactors. For more details on this subject, reference may be made to the publication "Réacteurs Chimiques" ["Chemical Reactors"] by P. Trambouze, published in Techniques de l'Ingénieur [Engineering Techniques] (J 4020, 12-1993), as well as to the publication "Selective oxidation in riser reactor" by R.M. Contractor and A.W. Sleight, published in Catalysis Today (vol. 3 (1988), 175-184), relating more particularly to transported bed reactors.

The reaction temperature is generally from 100 to 400°C, preferably from 150 to 350°C.

The total pressure of the gaseous reaction mixture is generally from 0.1 to 20 bar absolute.

The gas flow rate is generally set such that the contact time, calculated under standard temperature and pressure conditions, is from 0.1 to 30 seconds.

The contact time is preferably from 0.5 to 20 seconds. It is reminded that the contact time corresponds to the ratio between the volume of the reactor and the total flow rate of the gases.

The carboxylic acid formed is separated from the by-products or from the reactants in a conventional manner by cooling and condensation of an acid/water mixture.

The compounds remaining in gaseous form, more particularly the alkane and the carbon oxides, may, in an entirely advantageous manner, be recycled into the reactor. Recycling of the alkane is of entirely obvious advantage to a person skilled in the art; this advantage being to minimize the losses of this reactant. It should, however, be noted that recycling of the alkane and the carbon oxides has an additional advantage, relating to the absorption of calories released during the oxidation reaction. Indeed, these gases

have considerable calorific capacities which make them particularly suitable for this purpose and, consequently, the fact that they are recycled makes it possible to minimize the risks of a local increased of the temperature (hot spots).

In the case of recycling of these gases, and more especially as regards the carbon oxides, it is entirely evident to those skilled in the art that it is necessary regularly to purge these gases, which may well accumulate in the course of the recycling operations.

The composition according to the invention will now be described.

This composition is obtained from titanium dioxide as support and from a heteropolyacid of formula (I) as described above.

According to a preferred variant of the invention, the formula of the heteropolyacid corresponds to the formula (I) in which D is phosphorus, E is vanadium, c is from 1 to 3 inclusive, d is 1, and the sum $c + e$ is 12.

The titanium oxide present in the catalyst used in the process of the invention may without preference be in the form of anatase, rutile, brookite or alternatively bronze TiO_2 (symbolized (B)), or mixtures thereof.

The allotropic form of the titanium oxide is preferably chosen from the anatase and rutile forms or mixtures thereof.

The titanium oxide used in the composition of the active phase generally has a specific surface, measured according to the B.E.T. method, from 1 to 150 m^2/g . The specific surface is more particularly from 10 to 120 m^2/g .

The composition according to the invention is more particularly such that the atomic proportion $(C + E)/\text{Ti}$ is from 0.1 to 30% and preferably from 5 to 20%.

The subject of the invention is, moreover, a catalyst whose active phase is the composition described above.

According to a particular embodiment, the catalyst according to the invention comprises an inert material, besides the active phase obtained from titanium oxide and on heteropolyacid of formula (I).

heteropolyacid of formula (I).

A first variant consists of a catalyst of coated type. In this case, the amount of composition according to the invention is from 0.1 to 30% by weight, relative to the total weight of catalyst. The content is preferably from 2 to 20% by weight.

A second variant consists of a catalyst whose active phase is dispersed in the inert material. According to this variant, the amount of composition is from 1 to 90 % by weight, relative to the total weight of the catalyst.

All of that which has been mentioned above regarding the heteropolyacid, the inert material, the proportions of the various elements in relation to each other, and the modes of preparation of the catalyst, remains valid for this part and will thus not be repeated here.

The present invention will now be further described in the following Examples.

EXAMPLES

In the following text, the performances of the catalysts are calculated in the following way:

The conversion is calculated from the sum of the yields of products observed.

- Conversion of the ethane (% mol)

$$\text{conv. ethane} = \frac{\text{\texttt{E nbr of moles of products X observed}}}{\text{\texttt{(nbr. moles of ethane entered)}}} \times 100$$

- selectivity for a product X (acetic acid, ethylene, combustion products) (mol %)

$$\text{sel. X} = \frac{\text{\texttt{nbr of moles of product X}}}{\text{\texttt{E nbr of moles of products X observed}}} \times 100$$

EXAMPLE 1

Synthesis of a heteropolyacid of formula $H_5PMo_{11}VO_{40}/TiO_2$
(Catalyst 1):

8.23 g of MoO_3 , 0.52 g of V_2O_5 and 0.66 g of 85 % H_3PO_4 are mixed together in 150 ml of distilled water. After refluxing for 24 hours, 30 g of anatase TiO_2 (DT 51, Rhône-Poulenc - 86 m²/g) are added to the purple-red solution and the mixture is evaporated to dryness under vacuum.

The product is calcined at 320°C under air for 4 hours.

A catalyst is obtained for which the proportion (Mo + V)/Ti is 16.7 %.

³¹P magic angle Nuclear Magnetic Resonance analysis was carried out (unit: shift in ppm relative to an external reference of aqueous 85 % H_3PO_4 solution). This analysis makes it possible to confirm that the structure of the HPA is at least partially retained.

This technique gives signals between -3 and -4 ppm (singlet) for the bulk HPA in weak interaction with the TiO_2 support; at about +2 ppm (singlet) for the HPA in strong interaction with the TiO_2 support; between -10 and -15 ppm (broad poorly resolved signal) for the decomposed HPA. It should be noted that the presence of a signal between -3 and -4 ppm after synthesis of the catalyst is important in order to obtain good catalytic performances.

EXAMPLE 2

Synthesis of a heteropolyacid of formula $H_5PMo_{10}V_2O_{40}$ (Catalyst 2):

The sodium salts of the various constituents are used in the following proportions:

- 1 mol of $Na_2MoO_4 \cdot 2H_2O$ (242.0 g),
- 0.4 mol of $NaVO_3$ (48.8 g),
- 0.1 mol of Na_2HPO_4 (14.1 g).

- a) $NaVO_3$ is dissolved in 500 ml of boiling water. Na_2HPO_4 is added and the mixture is left to cool.
- b) $Na_2MoO_4 \cdot 2H_2O$ is dissolved in 500 ml of cold water.

- c) Solution a) is acidified with 37 % HCl until a purple-red colour is obtained, and solution b) is then added rapidly thereto, followed by dropwise addition of 400 ml of 37 % HCl while cooling in an ice bath.
- d) The etherate of the acid $H_5PMo_{10}V_2O_{40}$ is collected by extraction of solution c) with ether.

3 phases in the separating funnel:

lower: etherate of the acid,
middle: orange-coloured aqueous phase,
upper: ether.

The etherate is hydrolysed using half its volume of water and the mixture is left to crystallize at 4°C.

The crystals of $H_5PMo_{10}V_2O_{40} \cdot nH_2O$ obtained are calcined at 320°C under air.

EXAMPLE 3

Synthesis of a heteropolyacid of formula $H_5PMo_{10}V_2O_{40}/TiO_2$ (Catalyst 3):

9.08 g of the heteropolyacid obtained in Example 2 are dissolved in 150 ml of water with 14 g of 50 % H_2O_2 .

30 g of TiO_2 in anatase form (DT 51, Rhône-Poulenc - 86 m²/g) are then added and the mixture is evaporated to dryness under vacuum.

The product is dried for 16 hours at 140°C and then calcined under air at 320°C for 4 hours.

A catalyst is obtained for which the proportion (Mo + V)/Ti is 16.7 %.

EXAMPLE 4

Synthesis of a heteropolyacid of formula $H_5PMo_9V_3O_{40}$ (Catalyst 4):

The same procedure as that described in Example 2 is used, with the following proportions:

- 0.45 mol of $Na_2MoO_4 \cdot 2H_2O$ (108.90 g),
- 0.6 mol of $NaVO_3$ (73.20 g),
- 0.1 mol of Na_2HPO_4 (14.2 g).

A catalyst is obtained for which the proportion

(Mo + V)/Ti is 16.7%.

EXAMPLE 5 Comparative

Synthesis of a heteropolyacid of formula $H_3PMo_{12}O_{40}/TiO_2$:
(Catalyst 5)

The process is performed as described in Example 3, using commercial $H_3PMo_{12}O_{40} \cdot nH_2O$ (Fluka).

The product is calcined at 320°C under air for 4 hours.

A catalyst is obtained whose proportion Mo/Ti is 16.7%.

EXAMPLE 6

This example illustrates the performances of the catalysts described above in the reaction for the controlled oxidation of ethane into acetic acid.

3 g of catalyst powder are introduced into a stainless steel fixed bed continuous reactor equipped with heating via a bath of fluidized sand and with two chromatographs in series, one operating with a flame ionization detector and the other with a thermoconductimetric detector.

The feed gases are controlled by mass flowmeters.

The feed flow (expressed in mol %) consists of:

ethane/O₂/N₂ = 85/5/10.

The hourly volume rate is 3200 h⁻¹.

The pressure of the reactor is kept constant at 1 or 11 bar absolute.

The temperature is 250°C.

Catalyst	P (bar absolute)	conv. ethane (%)	sel. AcOH (%)	sel. C ₂ H ₄ (%)	sel. CO ₂ (%)
1	1	0.5	69	21	10
2	11	0.5	65	30	5
3	1	0.6	61	26	13
4	11	0.4	78	17	5
5	1	0.1	50	39	11

It is reminded that the theoretical conversion of ethane into acetic acid is 3.9%.

EXAMPLE 7

This Example illustrates the performance of the catalyst no. 1.

The conditions of reaction are those described in Example 6 except that the feed flow (expressed in mol %) consists of:

ethane/O₂/H₂O/N₂ = 62/17/10/11

The hourly volume rate is 2400 h⁻¹.

The pressure of the reactor is of 6 bar absolute.

The temperature is 275°C.

In such conditions, the conversion of ethane is 7.7%.

The selectivity of acetic acid is 70%, the selectivity of ethylene is 10% and the selectivity of CO_x is 20%.

CLAIMS

1. A process for the preparation of aliphatic carboxylic acids by controlled oxidation of the corresponding alkanes with a source of oxygen, in the presence of a catalyst whose active phase is obtained from a heteropolyacid of formula (I): $[A_xB_y]_z[C_cD_dE_eO_x]^{f-}$ in which:

- A represents at least one monovalent cation chosen from hydrogen, an alkali metal or the ammonium ion;

- B represents VO^{2+} , VO^{3+} , an alkaline-earth metal ion or an ion of a metal of groups VII A, VIII, I B, IV B and V B of the Periodic Table of the Elements;

- C represents Mo and/or W;

- D represents phosphorus, arsenic, antimony, silicon, germanium and/or boron;

- E represents vanadium and optionally at least one metal element chosen from groups V A, VII A and VIII or chromium;

- $f = a + \alpha b$ with α depending on the charge of the ion B, which is equal to 2, 3 or 4;

- c is from 5 to 20-e inclusive;

- d is from 1 to 5 inclusive; and

- e is from 1 to 9 inclusive.

2. A process according to claim 1, in which D is phosphorus, E is vanadium, c is from 1 to 3, d is 1 and the sum $c + e$ is 12.

3. A process according to claim 1 or 2, wherein the reaction is carried out in the presence of a catalyst whose active phase also comprises a support.

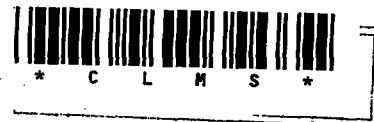
4. A process according to claim 4, wherein the support is chosen from titanium, silicon, zirconium, cerium and tin dioxides, alumina and silica-alumina, or mixtures thereof.

5. A process according to any one of the preceding claims, wherein the reaction is carried out with a gas mixture comprising 0.1 to 99.9 mol% of alkane.

6. A process according to claim 5 wherein the reaction is carried out with a gas mixture comprising 0.1 to 3 mol% or 10 to 99 mol% of alkane.

7. A process according to any one of the preceding





claims wherein air, oxygen or nitrous oxide is used as a source of oxygen.

8. A process according to claim 7, wherein the reaction is carried out with a gaseous mixture comprising 0.1 to 99.9 mol% of oxygen.

9. A process according to claim 8 wherein the reaction is carried out with a gaseous mixture comprising 1 and 90 mol% or 97 to 99.9 mol% of oxygen.

10. A process according to any one of the preceding claims, wherein a gaseous mixture having an alkane:oxygen molar ratio of less than 20:1 is used.

11. A process according to claim 10 wherein the alkane:oxygen molar ratio is from 0.01:1 to 0.2:1 or from 0.6:1 to 18:1.

12. A process according to any one of the preceding claims, wherein the reaction is carried out in the presence of a diluent chosen from water, an inert gas or a gas recycled from the reaction, alone or as a mixture.

13. A process according to claim 12, wherein a gaseous mixture comprising water as diluent is used.

14. A process according to any one of the preceding claims, wherein a gaseous mixture comprising 0 to 70 mol% of water as diluent is used.

15. A process according to claim 14 wherein a gaseous mixture comprising 0 to 20 mol% of water is used.

16. A process according to any one of claims 12 to 15, wherein a gaseous mixture comprising an inert gas chosen from rare gases or nitrogen is used as diluent.

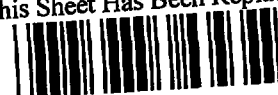
17. A process according to any one of the preceding claims wherein a gaseous mixture comprising 0 to 70 mol% of inert gas is used.

18. A process according to claim 17 wherein a gaseous mixture comprising 0 to 20 mol% of inert gas is used.

19. A composition comprising a titanium dioxide support and a catalyst whose active phase is obtained from a heteropolyacid of formula (I) as defined in claims 1 to 2.

20. A composition according to claim 19, wherein the titanium dioxide is in anatase, rutile, brookite or bronze form or a mixture thereof.

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21. A composition according to claims 19 or 20, wherein the atomic proportion $(C + E)/Ti$ is from 0.1 to 30%.
22. A composition according to claim 21 wherein the amount is from 5 to 20%.
23. A catalyst which comprises, as active phase, a composition as defined in any one of claims 19 to 22.
24. A catalyst according to claim 23, which comprises an inert material.
25. A catalyst according to claim 24, wherein the composition is coated on an inert material and the amount of the composition is from 0.1 to 30% by weight, relative to the total weight of catalyst.
26. A catalyst according to claim 25 wherein the amount of the composition is from 2 to 20% by weight.
27. A catalyst according to claim 24, wherein the composition is dispersed in an inert material and the amount of the composition is from 1 to 90% by weight, relative to the total weight of the catalyst.
28. Use of a catalyst as defined in any one of claims 24 to 27 in the preparation of aliphatic carboxylic acids by controlled oxidation of the corresponding alkanes with a source of oxygen.
29. An aliphatic carboxylic acid whenever prepared by a process as defined in any one of claims 11 to 18.



ABSTRACTHETEROPOLYACID-BASED CATALYSTS AND USE THEREOF
FOR THE PREPARATION OF ALIPHATIC CARBOXYLIC ACIDS

A process for the preparation of aliphatic carboxylic acids by controlled oxidation of the corresponding alkanes with a source of oxygen, in the presence of a catalyst whose active phase is obtained from a heteropolyacid of formula (I):

$[A_x B_y]_z [C_d D_e O_x]^{z-}$ in which:

- A represents at least one monovalent cation chosen from hydrogen, an alkali metal or the ammonium ion;
- B represents VO^{2+} , VO^{3+} , an alkaline-earth metal ion or an ion of a metal of groups VII A, VIII, I B, IV B and V B of the Periodic Table of the Elements;
- C represents Mo and/or W;
- D represents phosphorus, arsenic, antimony, silicon, germanium and/or boron;
- E represents vanadium and optionally at least one metal element chosen from groups V A, VII A and VIII or chromium;
- $f = a + \alpha b$ with α depending on the charge of the ion B, which is equal to 2, 3 or 4;
- c is from 5 to 20-e inclusive;
- d is from 1 to 5 inclusive; and
- e is from 1 to 9 inclusive.



HETEROPOLYACID-BASED CATALYSTS AND USE THEREOF
FOR THE PREPARATION OF ALIPHATIC CARBOXYLIC ACIDS

The present invention relates to a process for the preparation of carboxylic acids by controlled oxidation of the corresponding alkanes, in the presence of a catalyst whose active phase is obtainable from a heteropolyacid.

The present invention moreover relates to a ~~composition obtained from a heteropolyacid and titanium dioxide, as support, as well as to a catalyst comprising the said composition as active phase.~~

By convention, the term heteropolyacid (or HPA) will be used in this text to denote both heteropolyacids and polyoxometallates.

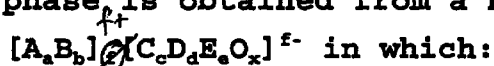
The production of carboxylic acids, in particular acetic acid, by controlled oxidation of the alkane, such as ethane, is a process in full development since it has the advantage of using a starting material which is of very competitive cost compared with those used in existing technologies.

Among the known processes of this type, there may be mentioned those using, besides ethane and oxygen, catalysts based, at least, on the vanadium, phosphorus and rhenium oxides. The selectivities towards acetic acid are of the order of 30 % but they remain, however, lower than those of the ethylene coproduced. In addition, this process requires the introduction into the reactor of large amounts of water and of an inert gas such as helium or nitrogen.

Another process consists in reacting the ethane and oxygen in the presence of catalysts based on at least a mixture of the molybdenum, vanadium, niobium and antimony oxides, or alternatively based on the molybdenum, vanadium, rhenium, antimony, niobium and calcium oxides. The selectivity towards acetic acid by the use of such catalysts is enhanced relative to that obtained according to the above process. However, the reaction conditions are demanding. Indeed, it is necessary to carry out the oxidation under conditions combining an elevated temperature, that is to say of the order of 300 to 400°C, and a high pressure, of the

hydrocarbons or alternatively given the reactivity of saturated hydrocarbons relative to unsaturated hydrocarbons, which may or may not be aromatic.

Thus, the process according to the invention comprises the preparation of aliphatic carboxylic acids by controlled oxidation of the corresponding alkanes, with a source of oxygen, in the presence of a catalyst whose active phase is obtained from a heteropolyacid of formula (I):



- A represents at least one monovalent cation chosen from hydrogen, an alkali metal or the ammonium ion;
- B represents VO^{2+} , VO^{3+} , an alkaline-earth metal ion or an ion of a metal of groups VII A, VIII, I B, IV B and V B of the Periodic Table of the Elements;
- C represents W and/or Mo;
- D represents phosphorus, arsenic, antimony, silicon, germanium or boron;
- E represents vanadium and optionally at least one metal element chosen from groups V A, VII A and VIII or chromium;
- $f = a + \alpha b$; with α depending on the charge of the ion B, which is equal to 2, 3 or 4;
- c is from 5 to 20-e inclusive;
- d is from 1 to 5 inclusive; and
- e is from 1 to 9 inclusive.

Here and for all of the description, the comments relating to the Periodic Table of the Elements refer to the table published in the supplement to the bulletin of the French Chemical Society (No. 1 - January 1966).

~~The subject of the invention is similarly a composition comprising a titanium dioxide as support and a catalyst whose active phase is obtained from a heteropolyacid of formula (I) $[A_a B_b]^{f+} [C_c D_d E_e O_x]^{f-}$ in which A, B, C, D, E, a, b, c, d, e and f have the same meanings as those given above.~~

~~Another subject of the invention consists of a catalyst which comprises, as active phase, the abovementioned composition.~~

A further subject of the present invention is the use of a catalyst as defined above in the preparation of



aliphatic carboxylic acids by controlled oxidation of the corresponding alkanes with a source of oxygen.

An additional subject of the present invention is an aliphatic carboxylic acid whenever prepared by a process as defined above.

In the text which follows, the terms titanium dioxide and titanium oxide have the same meaning.

More particularly, the element B is chosen from VO^{2+} , VO^{3+} , Cu^{2+} , Fe^{3+} , Co^{2+} , Ag^+ , Ni^{2+} , Mn^{2+} , Mg^{2+} , Bi^{3+} , Sn^{2+} and Sn^{4+} ions.

The element B is preferably chosen from the VO^{2+} and VO^{3+} ions.

As regards the element E which is other than vanadium, this is more particularly chosen from chromium, manganese, iron, cobalt and nickel.

According to a preferred variant of the invention, the heteropolyacid entering into the preparation of the active phase corresponds to the formula (I) in which D is phosphorus, E is vanadium, d is 1, ~~e is from 1 to 3~~ and the sum $c + e$ is 12.

According to a particular embodiment, the catalyst employed has an active phase which also comprises a support.

By way of support suitable for implementing this particular embodiment, there may, for example, be mentioned the titanium, silicon, zirconium, cerium and tin dioxides, alumina and silica-alumina, it being possible for these compounds to be used alone or as a mixture.

The support is preferably chosen from titanium dioxide and zirconium dioxide, the former being preferred.

According to a variant of this embodiment, the active phase of the catalyst has an atomic proportion $(C + E)/\text{metal element}$ of the support of from 0.1 to 30 %. The term metal element of the support refers to the titanium, zirconium, cerium, etc.

The abovementioned atomic ratio is preferably from 5 to 20%.

In the case where the active phase comprises a support, the distribution between the two constituents of the active phase is such that the heteropolyacid of formula (I)

CLAIMS

1. A process for the preparation of aliphatic carboxylic acids by controlled oxidation of the corresponding alkanes with a source of oxygen, in the presence of a catalyst whose active phase is obtained from a heteropolyacid of formula (I): $[A_x B_y]^{f+} [C_e D_d E_e O_x]^{f-}$ in which:

- A represents at least one monovalent cation chosen from hydrogen, an alkali metal or the ammonium ion;

- B represents VO^{2+} , VO^{3+} , an alkaline-earth metal ion or an ion of a metal of groups VII A, VIII, I B, IV B and V B of the Periodic Table of the Elements;

- C represents Mo and/or W;

- D represents phosphorus, arsenic, antimony, silicon, germanium and/or boron;

- E represents vanadium and optionally at least one metal element chosen from groups V A, VII A and VIII or chromium;

- $f = a + \alpha b$ with α depending on the charge of the ion B, which is equal to 2, 3 or 4;

- c is from 5 to 20-e inclusive;

- d is from 1 to 5 inclusive; and

- e is from 1 to 9 inclusive.

2. A process according to claim 1, in which D is phosphorus, E is vanadium, ~~e is from 1 to 3~~, d is 1 and the sum $c + e$ is 12.

3. A process according to claim 1 or 2, wherein the reaction is carried out in the presence of a catalyst whose active phase also comprises a support.

4. A process according to claim 4, wherein the support is chosen from titanium, silicon, zirconium, cerium and tin dioxides, alumina and silica-alumina, or mixtures thereof.

5 to 11
See below.

12. A process according to any one of the preceding claims, wherein the reaction is carried out with a gas mixture comprising 0.1 to 99.9 mol% of alkane.

13. A process according to claim 12 wherein the reaction is carried out with a gas mixture comprising 0.1 to 3 mol% or 10 to 99 mol% of alkane.

14. A process according to any one of the preceding



claims wherein air, oxygen or nitrous oxide is used as a source of oxygen.

15 ~~8~~¹⁴. A process according to claim ~~7~~¹⁴, wherein the reaction is carried out with a gaseous mixture comprising 0.1 to 99.9 mol% of oxygen.

16 ~~8~~¹⁵. A process according to claim ~~8~~¹⁵ wherein the reaction is carried out with a gaseous mixture comprising 1 and 90 mol% or 97 to 99.9 mol% of oxygen.

17 ~~10~~. A process according to any one of the preceding claims, wherein a gaseous mixture having an alkane:oxygen molar ratio of less than 20:1 is used.

18 ~~11~~¹⁷. A process according to claim ~~10~~¹⁷ wherein the alkane:oxygen molar ratio is from 0.01:1 to 0.2:1 or from 0.6:1 to 18:1.

19 ~~12~~. A process according to any one of the preceding claims, wherein the reaction is carried out in the presence of a diluent chosen from water, an inert gas or a gas recycled from the reaction, alone or as a mixture.

20 ~~13~~¹⁹. A process according to claim ~~12~~¹⁹, wherein a gaseous mixture comprising water as diluent is used.

21 ~~14~~. A process according to any one of the preceding claims, wherein a gaseous mixture comprising 0 to 70 mol% of water as diluent is used.

22 ~~15~~²¹. A process according to claim ~~14~~²¹ wherein a gaseous mixture comprising 0 to 20 mol% of water is used.

23 ~~16~~²². A process according to any one of claims ~~12~~¹⁹ to ~~15~~²¹, wherein a gaseous mixture comprising an inert gas chosen from rare gases or nitrogen is used as diluent.

24 ~~17~~. A process according to any one of the preceding claims wherein a gaseous mixture comprising 0 to 70 mol% of inert gas is used.

25 ~~18~~²⁴. A process according to claim ~~17~~²⁴ wherein a gaseous mixture comprising 0 to 20 mol% of inert gas is used.

~~19. A composition comprising a titanium dioxide support and a catalyst whose active phase is obtained from a heteropolyacid of formula (I) as defined in claims 1 to 2.~~

26 ~~composition~~^{process}. A ~~composition~~^{process} according to claim ~~19~~²⁴, wherein the titanium dioxide is in anatase, rutile, brookite or bronze form or a mixture thereof.



^{process}
621. A ~~composition~~ according to claims ⁴19 or ⁵20,
wherein the atomic proportion (C + E)/Ti is from 0.1 to 30%.

^{process}
122. A ~~composition~~ according to claim ⁶21 wherein the
amount is from 5 to 20%.

~~23. A catalyst which comprises, as active phase, a
composition as defined in any one of claims 19 to 22.~~

^{process}
wherein the catalyst ^{any one of the preceding claims}
824. A ~~catalyst~~ according to ¹claim ~~23~~, which
comprises an inert material.

^{process}
^{catalyst}
925. A ~~catalyst~~ according to claim ⁸24, wherein the
~~composition~~ is coated on an inert material and the amount of
^{active phase}
the ~~composition~~ is from 0.1 to 30% by weight, relative to the
total weight of catalyst.

^{process}
1026. A ~~catalyst~~ according to claim ⁹25 wherein the
amount of the composition is from 2 to 20% by weight.

^{process}
^{catalyst}
1127. A ~~catalyst~~ according to claim ⁸24, wherein the
~~composition~~ is dispersed in an inert material and the amount
^{active phase}
of the ~~composition~~ is from 1 to 90% by weight, relative to
the total weight of the catalyst.

2628. Use of a catalyst as defined in any one of
claims 24⁸ to 27¹¹ in the preparation of aliphatic carboxylic
acids by controlled oxidation of the corresponding alkanes
with a source of oxygen.

2729. An aliphatic carboxylic acid whenever prepared
by a process as defined in any one of claims ¹⁸11 to ²⁵18.

HETEROPOLYACID-BASED CATALYSTS AND USE THEREOF
FOR THE PREPARATION OF ALIPHATIC CARBOXYLIC ACIDS

The present invention relates to a process for the preparation of carboxylic acids by controlled oxidation of the corresponding alkanes, in the presence of a catalyst whose active phase is obtainable from a heteropolyacid.

By convention, the term heteropolyacid (or HPA) will be used in this text to denote both heteropolyacids and polyoxometallates.

The production of carboxylic acids, in particular acetic acid, by controlled oxidation of the alkane, such as ethane, is a process in full development since it has the advantage of using a starting material which is of very competitive cost compared with those used in existing technologies.

Among the known processes of this type, there may be mentioned those using, besides ethane and oxygen, catalysts based, at least, on the vanadium, phosphorus and rhenium oxides. The selectivities towards acetic acid are of the order of 30 % but they remain, however, lower than those of the ethylene coproduced. In addition, this process requires the introduction into the reactor of large amounts of water and of an inert gas such as helium or nitrogen.

Another process consists in reacting the ethane and oxygen in the presence of catalysts based on at least a mixture of the molybdenum, vanadium, niobium and antimony oxides, or alternatively based on the molybdenum, vanadium, rhenium, antimony, niobium and calcium oxides. The selectivity towards acetic acid by the use of such catalysts is enhanced relative to that obtained according to the above process. However, the reaction conditions are demanding. Indeed, it is necessary to carry out the oxidation under conditions combining an elevated temperature, that is to say of the order of 300 to 400°C, and a high pressure, of the

hydrocarbons or alternatively given the reactivity of saturated hydrocarbons relative to unsaturated hydrocarbons, which may or may not be aromatic.

Thus, the process according to the invention comprises the preparation of aliphatic carboxylic acids by controlled oxidation of the corresponding alkanes, with a source of oxygen, in the presence of a catalyst whose active phase is obtained from a heteropolyacid of formula (I):

$[A_x B_y]^{f+} [C_e D_d E_e O_x]^{f-}$ in which:

- A represents at least one monovalent cation chosen from hydrogen, an alkali metal or the ammonium ion;
- B represents VO^{2+} , VO^{3+} , an alkaline-earth metal ion or an ion of a metal of groups VII A, VIII, I B, IV B and V B of the Periodic Table of the Elements;
- C represents W and/or Mo;
- D represents phosphorus, arsenic, antimony, silicon, germanium or boron;
- E represents vanadium and optionally at least one metal element chosen from groups V A, VII A and VIII or chromium;
- $f = a + \alpha b$, with α depending on the charge of the ion B, which is equal to 2, 3 or 4;
- c is from 5 to 20-e inclusive;
- d is from 1 to 5 inclusive; and
- e is from 1 to 9 inclusive.

Here and for all of the description, the comments relating to the Periodic Table of the Elements refer to the table published in the supplement to the bulletin of the French Chemical Society (No. 1 - January 1966).

A further subject of the present invention is the use of a catalyst as defined above in the preparation of

aliphatic carboxylic acids by controlled oxidation of the corresponding alkanes with a source of oxygen.

An additional subject of the present invention is an aliphatic carboxylic acid whenever prepared by a process as defined above.

In the text which follows, the terms titanium dioxide and titanium oxide have the same meaning.

More particularly, the element B is chosen from VO^{2+} , VO^{3+} , Cu^{2+} , Fe^{3+} , Co^{2+} , Ag^+ , Ni^{2+} , Mn^{2+} , Mg^{2+} , Bi^{3+} , Sn^{2+} and Sn^{4+} ions.

The element B is preferably chosen from the VO^{2+} and VO^{3+} ions.

As regards the element E which is other than vanadium, this is more particularly chosen from chromium, manganese, iron, cobalt and nickel.

According to a preferred variant of the invention, the heteropolyacid entering into the preparation of the active phase corresponds to the formula (I) in which D is phosphorus, E is vanadium, d is 1, and the sum $c + e$ is 12.

According to a particular embodiment, the catalyst employed has an active phase which also comprises a support.

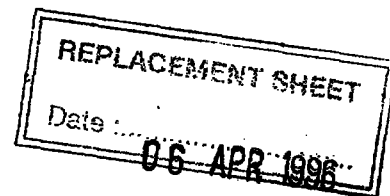
By way of support suitable for implementing this particular embodiment, there may, for example, be mentioned the titanium, silicon, zirconium, cerium and tin dioxides, alumina and silica-alumina, it being possible for these compounds to be used alone or as a mixture.

The support is preferably chosen from titanium dioxide and zirconium dioxide, the former being preferred.

According to a variant of this embodiment, the active phase of the catalyst has an atomic proportion $(C + E)/\text{metal element of the support}$ of from 0.1 to 30 %. The term metal element of the support refers to the titanium, zirconium, cerium, etc.

The abovementioned atomic ratio is preferably from 5 to 20%.

In the case where the active phase comprises a support, the distribution between the two constituents of the active phase is such that the heteropolyacid of formula (I)



CLAIMS

1. A process for the preparation of aliphatic carboxylic acids by controlled oxidation of the corresponding alkanes with a source of oxygen, in the presence of a catalyst whose active phase is obtained from a heteropolyacid of formula (I): $[A_xB_y]^{f+}[C_zD_eE_xO_x]^{f-}$ in which:

- A represents at least one monovalent cation chosen from hydrogen, an alkali metal or the ammonium ion;
- B represents VO^{3+} , VO^{3+} , an alkaline-earth metal ion or an ion of a metal of groups VII A, VIII, I B, IV B and V B of the Periodic Table of the Elements;
- C represents Mo and/or W;
- D represents phosphorus, arsenic, antimony, silicon, germanium and/or boron;
- E represents vanadium and optionally at least one metal element chosen from groups V A, VII A and VIII or chromium;
- $f = a + \alpha b$ with α depending on the charge of the ion B, which is equal to 2, 3 or 4;
- c is from 5 to 20-e inclusive;
- d is from 1 to 5 inclusive; and
- e is from 1 to 9 inclusive.

2. A process according to claim 1, in which D is phosphorus, E is vanadium, d is 1 and the sum $c + e$ is 12.

3. A process according to claim 1 or 2, wherein the reaction is carried out in the presence of a catalyst whose active phase also comprises a support.

4. A process according to claim 4, wherein the support is chosen from titanium, silicon, zirconium, cerium and tin dioxides, alumina and silica-alumina, or mixtures thereof.

5. A process according to claim 4, wherein the titanium dioxide is in anatase, rutile, brookite or bronze form or a mixture thereof.

6. A process according to claims 4 or 5, wherein the atomic proportion $(C + E)/Ti$ is from 0.1 to 30%.

7. A process according to claim 6 wherein the amount is from 5 to 20%.

8. A process according to any one of the preceding

claims wherein the catalyst comprises an inert material.

9. A process according to claim 8, wherein the catalyst is coated on an inert material and the amount of the active phase is from 0.1 to 30% by weight, relative to the total weight of catalyst.

10. A process according to claim 9 wherein the amount of the composition is from 2 to 20% by weight.

11. A process according to claim 8, wherein the catalyst is dispersed in an inert material and the amount of the active phase is from 1 to 90% by weight, relative to the total weight of the catalyst.

12. A process according to any one of the preceding claims, wherein the reaction is carried out with a gas mixture comprising 0.1 to 99.9 mol% of alkane.

13. A process according to claim 12 wherein the reaction is carried out with a gas mixture comprising 0.1 to 3 mol% or 10 to 99 mol% of alkane.

14. A process according to any one of the preceding claims wherein air, oxygen or nitrous oxide is used as a source of oxygen.

15. A process according to claim 14, wherein the reaction is carried out with a gaseous mixture comprising 0.1 to 99.9 mol% of oxygen.

16. A process according to claim 15 wherein the reaction is carried out with a gaseous mixture comprising 1 and 90 mol% or 97 to 99.9 mol% of oxygen.

17. A process according to any one of the preceding claims, wherein a gaseous mixture having an alkane:oxygen molar ratio of less than 20:1 is used.

18. A process according to claim 17 wherein the alkane:oxygen molar ratio is from 0.01:1 to 0.2:1 or from 0.6:1 to 18:1.

19. A process according to any one of the preceding claims, wherein the reaction is carried out in the presence of a diluent chosen from water, an inert gas or a gas recycled from the reaction, alone or as a mixture.

20. A process according to claim 19, wherein a gaseous mixture comprising water as diluent is used.

21. A process according to any one of the preceding

claims, wherein a gaseous mixture comprising 0 to 70 mol% of water as diluent is used.

22. A process according to claim 21 wherein a gaseous mixture comprising 0 to 20 mol% of water is used.

23. A process according to any one of claims 19 to 22, wherein a gaseous mixture comprising an inert gas chosen from rare gases or nitrogen is used as diluent.

24. A process according to any one of the preceding claims wherein a gaseous mixture comprising 0 to 70 mol% of inert gas is used.

25. A process according to claim 24 wherein a gaseous mixture comprising 0 to 20 mol% of inert gas is used.

26. Use of a catalyst as defined in any one of claims 8 to 11 in the preparation of aliphatic carboxylic acids by controlled oxidation of the corresponding alkanes with a source of oxygen.

27. An aliphatic carboxylic acid whenever prepared by a process as defined in any one of claims 18 to 25.