

**PROCESS FOR THE PREPARATION OF ACETIC ACID
BY CONTROLLED OXIDATION OF ETHANE**

The present invention relates to a process for the preparation of acetic acid by controlled
5 oxidation of ethane in the presence of a catalyst based especially on vanadium(V), titanium and oxygen.

Production of acetic acid by controlled oxidation of ethane in the presence of a catalyst is a process in full development because it offers the
10 advantage of employing a raw material which is advantageous in cost.

Among known processes of this type there may be mentioned those involving, besides ethane and oxygen, complex catalysts based on at least one mixture
15 of molybdenum, vanadium, niobium and antimony oxides. However, the selectivity for acetic acid when such catalysts are used is of the order of only 15 to 25 %, while the reaction conditions are relatively severe. In fact, the oxidation must be performed in conditions
20 combining an elevated temperature, that is to say of the order of 400°C, and a pressure of 20 bar.

Another process consists in reacting ethane and oxygen in the presence of a catalyst based at least on vanadium, tungsten and rhenium oxides. The
25 selectivities for acetic acid are improved in comparison with those of the catalysts described above (of the order of 30 %) but nevertheless remain lower than those for the ethylene which is also produced. In addition, this process requires large quantities of



water and of a diluent such as helium or nitrogen to be introduced into the reactor.

It is known, furthermore, to employ catalysts in which the active phase includes oxides of vanadium, the latter being in the (IV) oxidation state, of
5 titanium and/or of phosphorus. In the case of these catalysts the performance is advantageous in terms of selectivity for acetic acid. On the other hand, the reaction conditions make this process impossible to
10 exploit on an industrial scale. In fact, the ethane conversion is not high and the feed flow includes more than 90 % of diluent gas, and this results in a very low output efficiency.

As can be ascertained, at the present time
15 there are no processes for the preparation of acetic acid by ethane oxidation which can be developed on an industrial scale and which make use of catalysts of simple composition.

Now, it has been found quite unexpectedly
20 that the use of catalysts based on vanadium(V), titanium and oxygen in the abovementioned reaction makes it possible to mitigate the disadvantages referred to above.

The process according to the invention thus
25 combines an advantageous selectivity for acetic acid formed with an output efficiency which makes it possible to envisage an exploitation of the reaction on an industrial scale.

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An additional advantage of the process according to the invention lies in the very low ethane activation temperature. In fact, the conventional temperatures required for activating hydrocarbons in oxidation reactions such as the oxidation of propylene, ortho-xylene or butane are close to 400°C. Since it is known that olefins are more reactive than alkylaromatics, themselves being much more reactive than alkanes and that, moreover, the reactivity of saturated hydrocarbons increases with the number of carbon atoms present in the molecule, it is quite surprising to be capable of activating ethane at temperatures that can be as low as 150°C-250°C.

Furthermore, and this represents another advantage, the activation period of the catalyst used according to the invention is much shorter than for catalysts used in the conventional processes, this being due especially to a lower working temperature.

Furthermore, the catalyst used in the process according to the invention offers the advantage of being a catalytic composition of simple formulation, well known to a person skilled in the art, although being exploited in different applications.

These objectives, and others, are met by the present invention which therefore relates to a process for the preparation of acetic acid by a gas phase reaction of ethane and with a source of oxygen, in the presence of a catalyst in which the active phase



includes vanadium(V), titanium and oxygen.

For greater convenience the catalyst used in the invention will be described first of all.

As already indicated above, it has been found quite unexpectedly that the use of catalysts based on vanadium(V) and on titanium, as constituent elements of the active phase, is effective for obtaining acetic acid from ethane.

Thus, the active phase of the catalyst employed includes vanadium(V). The vanadium is preferably in the form of V_2O_5 .

The quantity of vanadium, expressed as V_2O_5 , in the active phase of the catalyst is between 0.1 and 30 % by weight. It should be noted that contents outside this range are not excluded, although they do not bring any additional advantages.

According to a more particular method of implementing the invention, the catalyst used in the present invention includes an active phase in which the vanadium content, expressed as V_2O_5 , is between 0.2 and 15 % by weight.

The titanium present in the active phase may be equally well in the form of anatase, rutile or brookite TiO_2 , or else bronze (symbolized as (B)), or their mixtures.

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

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The titanium oxide forming part of the composition of the catalytic phase additionally has a specific surface, measured by the B.E.T. method, of between 1 and 150 m²/g. More particularly, the specific surface is between 10 and 120 m²/g.

Furthermore, the active phase of the catalyst employed in the present invention may include at least one dopant.

The dopant is chosen from the following elements: K, Rb, Cs, Ca, Mg, Zr, Hf, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Cu, Ag, Zn, Cd, Tl, Si, Ge, Sn, P, As and Sb.

The dopant is preferably chosen from the following list: K, Cs, Zr, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Co, Pd, Ag, Zn, Tl, P and Sb.

The quantity of dopant in the active phase is usually lower than or equal to 1.5 atom% relative to vanadium.

The active phase of the catalyst used in the present invention may be obtained by any method known to a person skilled in the art.

It is possible, for example, to envisage manufacturing the said active phase by mixing the oxides of the elements of which the active phase consists, followed by a calcination stage, optionally followed and/or preceded by grinding of the said mixture (grog technique).

Another method which is suitable for the



preparation of the active phase consists in performing the following stages:

- a mixture is prepared based on at least one of the constituent elements of the active phase;
- the said elements are optionally precipitated;
- the optionally treated mixture is dried;
- the dried product is calcined.

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Constituent elements are intended to mean not only vanadium and titanium but also the dopant(s) added to the composition of the active phase.

The constituent elements are usually employed in the form of a solution or of a suspension.

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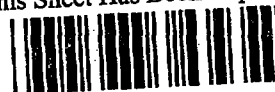
The dispersing (or solubilizing) medium is advantageously water, although any other type of dispersant (or solvent) can be envisaged. Alcohols such as methanol, ethanol, isopropanol and tert-butanol may be mentioned especially under this heading.

20

The constituent elements of the active phase forming part of the composition of the abovementioned mixture are generally employed in the form of salts of inorganic or organic acids or else in the form of compounds such as oxides or their derivatives.

25

All the acids or oxide derivatives indicated are suitable for the preparation of the mixture, insofar as they can decompose to an oxide of the corresponding element(s).



As examples of salts of inorganic acids which are suitable for the preparation of the abovementioned mixture there may be mentioned, among others, nitrates, sulphates, halides including one or more halogens, and ammonium salts.

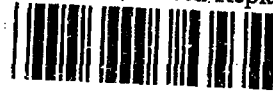
By way of examples of salts of organic acids or esters there may be mentioned the formate, oxalate, tartrate, acetate, acetylacetonate and ethylhexanoate.

As already indicated, it can also be envisaged to employ oxides or their derivatives, it being possible for these compounds to be employed in the form of particles, or dissolved, especially by adding an acid or a base to the said mixture.

Oxide derivatives are intended to mean the compounds of the oxyhalide, alkoxide, aryloxy and glycoxide type in particular.

It should be noted that all these compounds can be employed by themselves or mixed.

By way of examples of compounds containing vanadium and suitable for making use of this method of preparation there may be mentioned, without any limitation being intended, vanadyl sulphate, ammonium metavanadate and vanadium oxyhalides such as, especially, VOCl_3 , $(\text{VO}_2)\text{Cl}$, VOCl , VOBr , VOBr_2 , VOF_3 , VOF_2 , VF_4 , VBr_2 , VI_2 , vanadyl acetylacetonate, vanadyl oxalate, metavanadic acid, vanadium hexacarbonyl, vanadium oxide triisopropoxide and vanadium oxides such as, for example, V_2O_5 , V_7O_{13} , VO , VO_2 , V_2O_3 and V_3O_7 .



As titanium-containing compound there may be mentioned compounds of the TiX_4 type with X denoting a halogen and more particularly chlorine, and compounds of the $Ti(OR)_4$ type with R denoting an alkyl group and more particularly the ethyl, isopropyl or sec-butyl radicals.

Titanium oxide in its various allotropic forms, that is to say in anatase, rutile, brookite or (B) form is also suitable for making use of the invention.

With regard to the compounds based on a dopant, these are chosen from potassium chlorides, potassium acetate, rubidium chlorides, niobium chloride or oxychloride, niobium oxalate, caesium sulphate, caesium acetate, iron sulphate, iron acetate, chromium chlorides or chlorates, chromium nitrates, chromium acetate, chromium acetylacetonate, ammonium dimolybdate, ammonium metatungstate and paratungstate, oxides and alkoxides such as zirconium ethoxide, and silver oxide. This list cannot, of course, be considered to constitute a limit.

The temperature at which the mixing of the constituent elements is performed is usually between 20°C and the boiling temperature of the dispersant or solvent chosen.

In general, the concentration of the said mixture varies between 0.1 and 5 M.

According to a particular first embodiment a

stage of precipitation of at least one of the constituent elements present in dissolved form is performed next.

5 The said elements may be precipitated either simultaneously or successively. Furthermore, all or some of them can be precipitated during this operation.

10 In the latter case the first and second stages will be performed as many times as necessary for the product that is to be dried to contain all the constituent elements of the active phase.

15 Any kind of precipitating agent is suitable for making use of this stage insofar as it combines with one or a number of constituent elements in the form of a compound which is insoluble in the chosen mixture and insofar as the said insoluble compound makes it possible to gain access to the oxide of the combined element(s).

20 It should be noted that the precipitation can be carried out with one or a number of precipitating agents.

25 The said agent is conventionally chosen, among others, from bases particularly of the aqueous ammonia type, or from inorganic or organic acids such as hydrochloric acid or citric acid. It should be noted that water may constitute a precipitating agent which is suitable for making use of the invention. The choice of the precipitating agents is obviously not limited to this list alone, which is given by way of guidance.



The precipitation is usually carried out with stirring.

The temperature at which it is carried out generally varies between 20°C and the boiling
5 temperature of the solvent chosen.

Finally, the precipitation stage(s) may, if necessary, be followed by maturing stages. The latter consist in leaving the precipitate in suspension, with stirring, for a period varying approximately from
10 30 minutes to 4 hours.

The maturing temperature is within the temperature range indicated above.

Having been subjected to one or more precipitation stages, the mixture including the
15 constituent elements of the active phase is next dried.

A second embodiment of the process consists in drying the mixture without subjecting it beforehand to the precipitation stage described above.

According to a first alternative form the
20 drying is performed in two steps, the first consisting in evaporating the solvent or dispersant from the mixture, to dryness, the second in drying the paste thus obtained.

The first stage is generally carried out at a
25 temperature varying from 20 to 100°C for the period necessary to obtain a nonflowing paste.

The evaporation is usually performed with stirring.

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The resulting paste is next dried, in a second step, under a preferably nonreducing atmosphere such as, for example, oxygen or air, for an average period of 15 hours.

5 The drying temperature is usually approximately 120°C.

 According to a second alternative form the drying is performed by spraying the solution or suspension by any means known to a person skilled in
10 the art. Thus, without any limitation being intended, sprayers of the Buchi type or sprayers of "flash" type, as claimed in French patent applications published under the following numbers: 2 257 326, 2 419 754 and 2 431 321, are suitable for this embodiment.

15 The spraying temperature is generally of the order of 150 to 300°C.

 The atmosphere under which the spraying is performed, here again, is preferably nonreducing. The spraying is advantageously performed in air, although
20 oxygen can be envisaged for such a stage.

 The dried product obtained according to each of the abovementioned alternative forms is next subjected to a calcination stage.

 The latter is conventionally carried out
25 under a nonreducing atmosphere. Air is advantageously employed, but oxygen could be employed equally well.

 The calcination temperature is usually between 200 and 1200°C.

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The duration of the operation generally varies between 1 and 24 hours.

Before the calcination stage the dried product may undergo a grinding stage.

5 It should be noted that the calcined product may also be optionally subjected to such a treatment.

The catalyst used in the process according to the present invention may essentially include the active phase described above (bulk form) or may
10 additionally include a diluent (dilute form).

In the particular case where the catalyst includes a diluent (or support) the active phase may either be deposited on the latter or may coat it or else may be mixed with it.

15 The nature of the diluent is not critical, except that it must be inert towards the reactants in the reaction conditions which are chosen.

By way of materials capable of being employed as catalyst support there may be mentioned: silica,
20 alumina, silica-alumina, sintered clay, magnesia, magnesium silicate and diatomaceous earth. Supports of this type can be employed in porous or nonporous form. The support employed is preferably in nonporous form. If need be, a glazing of these may be performed in
25 order to make it such.

Ceramic materials, of the cordierite, alumina, mullite, porcelain, silicon nitride and boron and silicon carbide type may also be employed as a



diluent.

The catalyst used in the process according to the invention, whether diluted or not, is in the form of particles or of monolith.

5 In the case where the catalyst consists of particles, the particle size of the latter depends on the method of use of the catalyst. It may therefore vary within wide limits, such as, in particular, be between a few micrometres and about ten millimetres.

10 More particularly, and by way of guidance, a catalyst employed in a stationary bed has a particle size distribution which is generally between 0.5 and 6 mm. The particle size of the particles of a catalyst employed in a fluidized or moving bed is usually

15 between 5 and 700 microns and preferably between 5 and 200 microns for 80 % of the particles.

 The quantity of diluent forming part of the composition of the catalyst conventionally varies within wide limits depending, most of the time, on the

20 method of formation of the catalyst.

 Thus, catalysts obtained by coating or depositing the active phase on the support have a quantity of active phase which usually varies between 0.1 and 30 % and preferably between 2 and 20 % as total

25 weight of finished catalyst (active phase and support). In the cases where the catalyst includes a support dispersed in the active phase, the quantity of active phase is between 1 and 90 % as total weight of finished



catalyst.

According to a particular embodiment of the invention the reaction is carried out in the presence of a catalyst of coated type.

5 The catalyst according to the invention can be obtained by any conventional method known to a person skilled in the art.

Thus, bulk catalysts essentially including the active phase as defined above can be formed by
10 extrusion, by moulding, by grinding, crushing or any other means, of the active phase or of its precursor, so as to give a monolith or else particles of suitable particle size.

Here and throughout the remainder of the
15 description a precursor of the active phase is intended to mean the mixture of the elements of which this phase consists in all the states prior to the calcination stage described above.

In the case of catalysts including a diluent,
20 the means described above can be employed. The active phase can thus be mixed with the required proportion of diluent and, for example, the resulting mixture may be extruded or moulded.

However, other methods can be envisaged.

25 Thus, according to a first embodiment, the diluent, preferably in the form of rough particles, and the active phase or its precursor are placed in contact in a high-shear mixer (apparatus of Lodige type) or in

a granulating apparatus (pelletizers in the form of a drum or dish).

The operation is generally performed at a temperature which varies between 20 and 150°C throughout the period needed for coating the support with the desired quantity of active phase, more particularly under air, for at least 30 minutes.

The particles thus obtained are usually calcined at a temperature of between 300 and 600°C, preferably between 450 and 500°C.

The calcination period is generally at least 3 hours.

A second possible method of manufacture of the catalyst consists in applying the impregnation technique.

According to this technique the support is impregnated with a suspension of the active phase or with a suspension or solution of its precursor.

The impregnation stage is followed by a drying stage, usually performed at a temperature of between 100 and 200°C, under air, for at least 30 minutes.

The impregnation-drying cycle can then be renewed and the drying may be finished by calcining in air.

The calcination temperature is between 400 and 600°C for about ten hours.

A possible alternative form consists in



performing a calcination between the impregnation-drying cycle(s).

According to a third method of preparation of the catalyst, the support, preferably in the form of particles, is added to the mixture of at least one of the constituent elements of the active phase. The mixture thus obtained is then treated in accordance with the various embodiments of the process for the preparation of the catalyst phase, as described above.

All these methods of preparation are, of course, given merely by way of guidance and cannot in any event constitute an exhaustive list.

The present invention relates, furthermore, to a process for the preparation of acetic acid by a gas-phase reaction of ethane with a source of oxygen in the presence of a catalyst as defined above.

There are no special conditions relating to the quality of the ethane used. However, for obvious questions of separation of the acid formed, it is preferred to employ ethane which has a purity of at least 90 %.

This can be employed equally well by itself or diluted in a diluent gas which is inert in the conditions of the reaction. Rare gases such as especially helium or argon or else nitrogen are diluent gases which are suitable for making use of the process according to the invention.

The controlled oxidation reaction of ethane



is used in the presence of a source of oxygen. The latter may be based on oxygen which is pure or diluted in an inert gas. The oxidation reaction can thus be performed by employing air as a source of oxygen.

5 According to a particular embodiment of the present invention the molar ratio of ethane to oxygen is lower than 20. More particularly, this ratio is between 0.01 and 0.2 or between 0.6 and 15.

 According to a preferred method of the
10 invention the said ratio is between 0.6 and 15.

 An alternative form of the process consists in employing a gaseous mixture including water, besides the other constituents.

 The composition of the gaseous mixture, that
15 is to say ethane, the source of oxygen, the diluent gas if appropriate and water, may vary within wide limits.

 Unless stated otherwise, all the percentages shown in what follows are expressed as the total number of moles of the gaseous mixture.

20 In general, the ethane content in the gaseous mixture is between 0.1 and 99.9 %.

 According to a particular embodiment of the invention the composition of the gaseous mixture is such that it lies outside the region of explosiveness
25 of the said mixture.

 More particularly, and in order to have a gaseous mixture whose composition is conveniently outside the explosiveness region, the said ethane





content is between 0.1 and 3 % or between 10 and 99 %.

The ethane content in the abovementioned gaseous mixture is preferably between 10 and 99 %.

5 The oxygen content in the gaseous mixture used also varies within a wide range of concentration. It is, in fact, between 0.1 and 99.9 %.

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

10 The oxygen present in the said mixture is preferably between 1 and 90 %.

The water content in the gaseous mixture used is between 0 and 70 %.

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

The content of diluent gas in the mixture usually varies between 0 and 70 %.

20 More particularly, the mixture includes between 0 and 20 % of diluent gas.

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

25 The device in which the process according to the invention is used forms part of the conventional devices for gas-phase catalytic reactions, it being possible for these to be employed continuously or noncontinuously.

The reaction can thus be performed in the



presence of a catalyst in a stationary, fluidized or else transported bed.

The reaction temperature is generally situated between 100 and 400°C, preferably between 150
5 and 350°C.

The total pressure of the gaseous reaction mixture generally varies between 0.1 and 20 bar absolute.

The gas flow rate is set so that the contact
10 time, calculated under normal temperature and pressure conditions, is between 0.1 and 30 seconds. The contact time is preferably between 0.5 and 20 seconds. It should be remembered that the contact time corresponds to the ratio of the reactor volume to the total flow
15 rate of the gases.

The acetic acid formed is separated from the by-products or the reactants, conventionally by cooling and then condensing an acid/water mixture. The compounds which remain in gaseous form, more
20 particularly ethane, can be recycled to the reactor after having optionally been subjected to a separation stage.

Concrete but nonlimiting examples of the invention will now be presented.



EXAMPLE 1

Preparation of the V_2O_5 . TiO_2 /clay catalyst according to the invention (catalyst A)

90 g of TiO_2 (i.e. 1.125 mol), exhibiting a
5 BET surface of $86 \text{ m}^2/\text{g}$ (marketed by Rhône-Poulenc) are introduced into a pelletizer and impregnated dry with 100 cm^3 of a solution of vanadyl oxalate.

The solution employed includes 15.23 g of oxalic acid dihydrate (i.e. 120.8 mmol) and 6.77 g of
10 commercial V_2O_5 from Janssen (i.e. 37.2 mmol) in water.

The product thus obtained is calcined for 3 hours in air at 500°C .

The composition of the calcined product shows 7 % by weight of V_2O_5 and a V/Ti ratio of 0.066.

15 25 g of the active phase thus prepared are deposited on 100 g of clay beads with a mean diameter of 5 mm (marketed by Rhône-Poulenc) by coating in a pelletizer, with the aid of an aqueous solution of glucose.

20 The product is then calcined for 3 hours in air at 500°C .

The final active phase content of the catalyst is 17.4 % by weight.

EXAMPLE 2, COMPARATIVE

25 Preparation of the V_2O_5 /clay catalyst (catalyst B)

1.5 g of commercial V_2O_5 from Janssen are deposited on 100 g of clay beads with a mean diameter of 5 mm (marketed by Rhône-Poulenc) by coating in a



pelletizer, with the aid of an aqueous solution of glucose.

The product is then calcined for 3 hours in air at 500°C.

5 The final active phase content of the catalyst is 1.41 % by weight.

EXAMPLE 3, COMPARATIVE

Preparation of the TiO_2 /clay catalyst (catalyst C)

25 g of TiO_2 which has a BET surface of
10 86 m^2/g (marketed by Rhône-Poulenc) are coated in a pelletizer on 100 g of clay beads with a mean diameter of 5 mm (marketed by Rhône-Poulenc) with the aid of an aqueous solution of glucose.

The product is then calcined for 3 hours in
15 air at 500°C.

The final active phase content of the catalyst is 16.5 % by weight.

EXAMPLE 4, COMPARATIVE

Preparation of the $(\text{VO})_2\text{P}_2\text{O}_7$ /clay catalyst (catalyst D)

20 100 g of V_2O_5 (i.e. 550 mmol) are dissolved in a mixture of isobutyl (600 cm^3) and benzyl (400 cm^3) alcohols. The operation is performed at reflux (118°C) with stirring for 2 to 3 hours.

When the V_2O_5 has dissolved completely, the
25 stirring speed is increased and 145.8 g of phosphoric acid at a concentration of 85 % by weight (i.e. 1.27 mol) are added dropwise and refluxing is continued for 2 hours.

After cooling of the mixture thus obtained a blue precipitate is recovered. The latter is filtered on sintered glass and then dried for 3 hours in an oven at 110°C.

5 The resulting product consists of
(VO)HPO₄·0.5H₂O.

A calcination is then performed for 16 hours under nitrogen at 400°C.

10 The X-ray determination of the composition
obtained shows that it corresponds to the phase
(VO)₂P₂O₇.

3 g of the phase thus prepared are coated in a pelletizer according to the procedure shown in the preceding examples.

15 The solid is then dried for 6 hours in air at 110°C.

The final active phase content of the catalyst is 3.01 % by weight.

20 Before use in the ethane oxidation reaction
the catalyst is calcined in the reactor, in air, for 3 hours at 500°C.

EXAMPLE 5

25 This example illustrates the application of
the catalysts prepared above in a process for the
preparation of acetic acid from ethane.

The catalyst (20 cm³) is introduced into a stainless steel continuous reactor containing a stationary bed, equipped with heating using a fluidized



sand bath and two in-line chromatographs, one operating with a flame ionization detector and the other with a katharometer detector.

The feed gases are controlled by mass
5 flowmeters.

The water is introduced in liquid form (Gilson metering pump) into a vaporizer integrated into the gas circuit.

The feed flow consists of:
10 $C_2H_6/O_2/N_2/H_2O = 79.5/5.2/6.1/9.2$ mol%.

The total flow is 69.17 l/h under normal temperature and pressure conditions.

The hourly space velocity (HSV) is 3 500 h⁻¹, which corresponds to a contact time of approximately
15 1 second.

The reaction pressure is kept constant at 11 bar (absolute pressure).

The temperature is varied between 250 and 300°C.

20 The results obtained are collated in the following table.

In the latter the performance is calculated as follows:

- ethane conversion (mol%)

$$25 \quad \text{ethane conv.} = \frac{(\text{no. moles ethane in} - \text{no. moles ethane out})}{(\text{no. moles ethane in})} \times 100$$

- oxygen conversion (mol%)

$$30 \quad O_2 \text{ conv.} = \frac{(\text{no. moles } O_2 \text{ in} - \text{no. moles } O_2 \text{ out})}{(\text{no. moles } O_2 \text{ in})} \times 100$$



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

$$5 \quad X \text{ sel.} = \frac{\text{no. moles ethane converted to X}}{(\text{no. moles ethane in} - \text{no. moles ethane out})} \times 100$$

TABLE 1

Summary of the results of controlled oxidation of
ethane

Catalyst	T (°C)	Conv. (%)		Sel. (%)	
		C ₂ *	O ₂	AcOH	C ₂ H ₄
A	250	0.5	13	29	23
	260	0.9	26	27	21
	280	3.3	99	12	20
B	280	0			
C	280	0.1		0	33
D	280	0			

15 * The theoretical maximum conversion of ethane to acid as a function of the initial molar ratio and of the stoichiometry is equal to 4.4 %.





CLAIMS

1. Process for the preparation of acetic acid by a gas phase reaction of ethane with a source of oxygen, characterized in that the reaction is performed
5 in the presence of a catalyst in which the active phase is based on vanadium(V), titanium and oxygen.

2. Process according to the preceding claim, characterized in that a catalyst is employed in which the active phase includes titanium in the form of
10 anatase, rutile, brookite, TiO_2 , bronze or their mixtures.

3. Process according to one of the preceding claims, characterized in that a catalyst is employed in which the active phase includes titanium
15 which has a specific surface, measured by the B.E.T. method, of between 1 and 150 m^2/g and preferably between 10 and 120 m^2/g .

4. Process according to any one of the preceding claims, characterized in that a catalyst is
20 employed in which the active phase includes from 0.1 to 30 % by weight of vanadium, expressed as V_2O_5 , and preferably includes from 0.2 to 15 % by weight.

5. Process according to any one of the preceding claims, characterized in that a catalyst in
25 bulk or diluted form is employed.

6. Process according to the preceding claim, characterized in that a coated catalyst is employed including 0.1 to 30 % by weight of active





phase in relation to the total weight of finished catalyst, and preferably from 2 to 20 % by weight.

7. Process according to claim 5, characterized in that a catalyst is employed including
5 a support dispersed in the active phase, including 1 to 90 % of active phase relative to the total weight of the finished catalyst.

8. Process according to any one of the preceding claims, characterized in that a catalyst is
10 employed in which the active phase includes at least one dopant chosen from the following elements: K, Rb, Cs, Ca, Mg, Zr, Hf, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Cu, Ag, Zn, Cd, Tl, Si, Ge, Sn, P, As and Sb.

15 9. Process according to the preceding claim, characterized in that the dopant content is lower than or equal to 1.5 atom% relative to vanadium.

10. Process according to any one of the preceding claims, characterized in that the reaction is
20 performed with a gaseous mixture including 0.1 to 99.9 mol% of ethane and more particularly the said mixture includes between 0.1 and 3 % or between 10 and 99 mol% of ethane.

11. Process according to any one of the
25 preceding claims, characterized in that air or oxygen is employed as a source of oxygen.

12. Process according to the preceding claim, characterized in that the reaction is performed





with a gaseous mixture including 0.1 to 99.9 mol% of oxygen and more particularly including between 1 and 90 % or between 97 and 99.9 mol% of oxygen.

13. Process according to any one of the preceding claims, characterized in that a gaseous mixture is employed exhibiting an ethane/oxygen molar ratio lower than 20 and more particularly between 0.01 and 0.2 or between 0.6 and 15.

14. Process according to any one of the preceding claims, characterized in that a gaseous mixture including water is employed.

15. Process according to the preceding claim, characterized in that a gaseous mixture is employed including 0 to 70 mol% of water and preferably including 0 to 20 mol% of water.

16. Process according to any one of the preceding claims, characterized in that a gaseous mixture is employed including a diluent gas chosen from the rare gases or nitrogen.

17. Process according to the preceding claim, characterized in that a gaseous mixture is employed including 0 to 70 mol% of diluent gas and preferably including 0 to 20 mol% of the said gas.

18. Process according to any one of the preceding claims, characterized in that the reaction is performed at a temperature of between 100 and 400°C, preferably between 150 and 350°C.

19. Process according to any one of the





preceding claims, characterized in that the reaction is performed at a pressure of between 0.1 and 20 bar absolute.

20. Process according to any one of the
5 preceding claims, characterized in that the reaction is performed in conditions such that the contact time, calculated under normal temperature and pressure conditions, is between 0.1 and 30 seconds and preferably between 0.5 and 20 seconds.

This Sheet Has Been Replaced

