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## EUROPEAN QUALIFYING EXAMINATION 2000

### PAPER B CHEMISTRY

THIS PAPER COMPRISES:

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| * DESCRIPTION OF THE APPLICATION  | 2000/B(C)/E/1-8   |
| * COMMUNICATION                   | 2000/B(C)/E/9     |
| * DOCUMENT DI (STATE OF THE ART)  | 2000/B(C)/E/10-12 |
| * DOCUMENT DII (STATE OF THE ART) | 2000/B(C)/E/13-14 |

## DESCRIPTION OF THE APPLICATION

The present invention is directed to the gas-phase oxidation of hydrocarbons with oxygen or gases containing oxygen and to an improved catalyst for this process.

As in many of the previously known processes, our process comprises contacting hydrocarbons in the gas phase with oxygen or gases containing oxygen (such as air) in the presence of a catalyst. The catalysts employed in the known processes contain vanadium pentoxide and titanium dioxide in the anatase structure. Our process differs from the processes of the state of the art in that a different catalyst is employed.

The present oxidation catalyst is formed from  $V_2O_5$  (vanadium pentoxide) and rutile  $TiO_2$  (rutile titanium dioxide).

$TiO_2$  exists in three crystal structures, i.e. rutile, anatase and brookite. These structures can be easily distinguished by X-ray diffraction. Rutile  $TiO_2$  in the sense of the present invention is any  $TiO_2$  which contains at least 50 weight % of rutile, the remainder being anatase, brookite or amorphous  $TiO_2$ .

This catalyst proved to be more effective than the catalysts employed in the prior art where the titanium dioxide is of anatase structure.

Catalysts are normally assessed on the basis of their activity and selectivity for a given reaction. An enhanced activity is present when the conversion rate of the starting materials at a given temperature is increased (or when, for a given conversion, a lower temperature can be used). An enhanced selectivity is present when under set reaction conditions the desired product is present in a larger amount in the product stream.

## **PROBLEM**

It is an object of the present invention to provide a  $V_2O_5$  and  $TiO_2$  containing catalyst which has a high reactivity in industrial oxidation processes whilst maintaining or improving the selectivity towards desirable products.

## SOLUTION

These and further objects, which become more apparent in the following text, are achieved by an oxidation catalyst which comprises vanadium pentoxide and rutile titanium dioxide, the said catalyst  
5 containing 1-50% by weight of vanadium pentoxide and having a specific surface area in the range from 5 to 100 m<sup>2</sup>/g, and by a process wherein a hydrocarbon is oxidised in the gas phase with oxygen or oxygen containing gases in the presence of said catalyst.

### 10 THE CATALYST

The present catalyst may be produced by any process which ensures that the titanium oxide is rutile  
**TiO<sub>2</sub>**, the catalyst contains 1-50% of vanadium pentoxide and has a specific surface area in the range  
5 from 5 to 100 m<sup>2</sup>/g.

Specific surface area in the sense of the present invention means the BET-surface area, i.e. the surface  
area determined by nitrogen adsorption according to the method of Brunauer, Emmett and Teller.

One way of preparing such catalysts is by contacting a gaseous vanadium compound, such as  
1) vanadium oxytrichloride (**VOCl<sub>3</sub>**), with a rutile titanium dioxide support structure having an appropriate specific surface area and hydrolysing the **VOCl<sub>3</sub>** on said support to yield vanadium pentoxide. The **VOCl<sub>3</sub>** gas may be contacted once or several times with the rutile support. The hydrolysis of the vanadium compound is usually performed by heating it to a temperature of at least 250 °C in an air flow.

25

The catalyst may also be obtained by preparing a **TiO<sub>2</sub>** hydrogel, mixing it with an aqueous solution of **V(IV)** (see below), precipitating the vanadium oxide, spray-drying and calcining the resulting suspension.

30 Calcination means the heating of a solid substance in order to effect a physical or chemical change.

Finally, the catalyst may be obtained by a process comprising mixing an aqueous solution with an aqueous solution of V(IV) (see below), followed by coprecipitating the titanium and vanadium oxides, drying, oxidising and calcining the precipitate.

- 5 Ti(IV) and V(IV) mean titanium and vanadium in the oxidation state +4, as in, e.g.,  $\text{VO}^{2+}$  and  $\text{TiO}^{2+}$  and  $\text{TiCl}_4$ . The preparation of the V(IV) solution from  $\text{V}_2\text{O}_5$  implies the reduction of V(V) (i.e. vanadium in the oxidation state +5) e.g. of oxalic acid.

This process preferably comprises the following steps:

- 10 (a) preparation of a solution of Ti(IV) with a final pH below 1.0 by partial hydrolysis of  $\text{TiCl}_4$  in an aqueous solution,  
(b) preparation of a solution of V(IV) by dissolving solid  $\text{V}_2\text{O}_5$  suspended in an aqueous oxalic acid solution,  
(c) mixing solutions a) and b),  
5 (d) coprecipitation of vanadium and titanium oxides, and  
(e) separation of the precipitate obtained in (d), drying, oxidation and calcination thereof at temperatures above 250 °C.

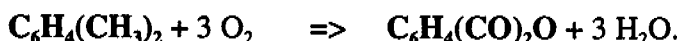
The coprecipitation of the vanadium and titanium compounds may, e.g., be effected by adding a base 7 to the solution containing V(IV) and Ti(IV). A suitable base is aqueous ammonia. The preferred calcination temperatures are from 250 °C to 1000 °C, preferably from 350 °C to 800 °C, especially from 400 °C to 700 °C, most preferably from 500 °C to 600 °C.

The catalyst contains from 1 to 50 % by weight of vanadium pentoxide, preferably from 10 to 35 %, 25 most preferably from 15 to 25 %.

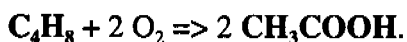
## THE HYDROCARBONS

The hydrocarbons to be oxidised in the present process are not limited as long as they are gaseous or 30 may be brought into the gaseous state at a reasonable temperature and/or pressure. The preferred hydrocarbons are o-xylene, naphthalene or butenes.

Ortho-xylene may be oxidised to yield phthalic anhydride:



The oxidation of a butene or a mixture of butenes with the present catalyst generally yields acetic acid:



### EXAMPLES

10 The experimental examples which follow are illustrative and do not restrict the scope of the invention. All the catalysts prepared according to these examples have a BET surface area within the range of from 5 to 100 m<sup>2</sup>/g.

#### Example 1

- 5
- (a) A rutile titanium dioxide was selected for use as the catalyst substrate. This rutile titanium dioxide had a specific surface area of 10 square meters per gram and was sieved to a particle size range of 200 to 300 micrometers.
- 7 (b) The catalyst substrate was then placed in a "U" shaped tube and a water vapour/air mixture was passed through the tube for two hours at 50 °C with a velocity of 20 cm<sup>3</sup> per minute (process step 1). Dry air at 140 °C was then passed through the tube for a further four hours to remove excess water from the catalyst substrate. The tube was then allowed to cool to room temperature and dry air containing vanadium oxytrichloride (VOCl<sub>3</sub>) vapour was passed through the tube overnight (process step 2). At the completion of this time the temperature of the tube was then raised slowly to 350 °C during which time dry air was passed through the tube to remove hydrogen chloride gas and to complete the hydrolysis of the vanadium oxytrichloride to vanadium pentoxide (process step 3).
- 25
- 30 The steps 1, 2 and 3 were carried out a total of 6 times.

The resulting catalyst was determined to contain 21.5 % by weight V<sub>2</sub>O<sub>5</sub>.

Example 2

- 5 (a) 10 g of  $V_2O_5$  (vanadium pentoxide) was suspended in a solution of oxalic acid (20.8 g in 200 of distilled water) in a three-necked flask; the suspension was heated to 70 °C until the  $V_2O_5$  had been completely reduced to V(IV). The reaction was complete when a clear blue solution was obtained. The time needed for the complete reduction was about 2 hours. The solution was cooled and any unreacted residues of  $V_2O_5$  were separated off by filtration.
- 10 (b) 50 cm<sup>3</sup> of  $TiCl_4$  were slowly added dropwise to a second flask containing a solution of HCl in  $H_2O$  (10 cm<sup>3</sup> of 37% HCl in 300 cm<sup>3</sup> of  $H_2O$ ). The solution was vigorously stirred and the flask was cooled in an ice bath during the partial hydrolysis of the  $TiCl_4$ .

The two solutions were then mixed whilst cold.

- 5 The precipitation was carried out by adding dropwise, with stirring, a solution of  $NH_4OH$  (30% of  $NH_3$ ) until a pH of 1.0 was obtained. An initial opalescence formed, and the precipitation was complete after about 12 hours.

- 10 The precipitate was dried at 80 °C for 24 hours and calcined at 350 °C for 3 hours. The  $TiO_2$  in the catalyst thus obtained was in the rutile crystal form, and the fraction of vanadium in the catalyst was 21.9%, expressed as % by weight of  $V_2O_5$ .

Example 3

- 25 (a) To 1500 g of a stirred 10% aqueous solution of titanium sulphate at 40 °C, 1700 g of 15% aqueous ammonia was added over a period of 10 minutes at a temperature of 40 °C. The resulting titanium oxide hydrogel was filtered, and was washed 3 times with water. The hydrogel was dried for 3 hours at 110 °C and subsequently for 18 hours at 250 °C.

(b) 199 g of vanadium pentoxide was suspended in 398 g of pure water, and heated with  
80 °C. Then 418 g of oxalic acid was gradually added to reduce the vanadium and form a  
vanadium (IV) oxalate solution. The formation of a homogeneous solution confirmed the  
complete reduction of vanadium. The solution was then cooled to 40 °C. The dried titanium  
oxide hydrogel obtained in step (a) was added with thorough stirring to the resulting vanadium  
(IV) oxalate solution, and the mixture was spray dried. The fine spherical particles obtained were  
calcined in a muffle furnace at 350 °C for 3 hours.

The resulting catalyst contained titanium oxide in the rutile crystal form and the fraction of vanadium  
in the catalyst was 20.2%, expressed as % by weight of  $V_2O_5$ .

#### Examples 4-8

Catalysts were prepared as in Example 2, but the solid product after drying was calcined at 450 °C for  
3 hours (Example 4), or at 500 °C for 3 hours (Example 5), or at 550 °C for 3 hours (Example 6) or at  
600 °C for 3 hours (Example 7) or at 650 °C for 3 hours (Example 8).

#### Example 9

The catalysts prepared by the procedure reported in the preceding examples were used for the  
gas-phase oxidation of o-xylene with air to phthalic anhydride.

The reaction was operated with an hourly space velocity of 5,000 hours<sup>-1</sup>, a projected conversion of  
99 %, and a projected selectivity to the anhydride of 50 %. The desired conversion was obtained at  
reaction temperatures between 290 and 330 °C.

In contrast commercially available catalysts which consist of about 21 % by weight of  $V_2O_5$  and  
anatase  $TiO_2$  require a reaction temperature of at least 360 °C to achieve a 99 % conversion at a  
selectivity to the anhydride of 50 %.

These data demonstrate the superiority of the catalysts which are the subject of the present invention  
and which show high activities at temperatures at least 30 °C lower than those used according to the  
state of the art. The present catalysts are thus commercially very attractive.

Example 10

300 g of catalyst sieved to 0.1 - 0.3 mm was introduced into a fluidised bed reactor having a diameter of 40 mm. 150 l/h of air, 10 l/h of n-butene and 100 l/h of steam were fed to the reactor. The internal temperature of the reactor was maintained at 315 °C. The effluent gas was cooled, thereby condensing the water and the acids which were be separated. The waste gas contained, in addition to oxides of carbon, unreacted butene. The catalysts of examples 1 - 8 and a commercial catalyst were tested. The butene conversions obtained as well as the selectivity to the individual reaction products are listed in the following table.

10

Catalyst according to

example no.

1   2   3   4   5   6   7   8   \*

Butene conversion (%)

80   85   90   85   85   80   78   75   40

Selectivity (weight percent of products +)

Acetic acid                      25   40   35   38   55   60   45   35   40

Propionic acid                    5   0.5   1.0   0.5   0.5   0.5   3   8   0.5

Formic acid                        0.5   0.0   0.5   0.3   0.5   0.0   4   6   0.0

Maleic acid                        7   8   6   6   4   2   0.0   0.0   5

25

Formaldehyde                    9   0.5   4   0.5   0.0   3   10   15   2

Oxides of carbon                43   45   48   47   35   21   25   40   48

30 \* Commercial catalyst (21 % by weight of V<sub>2</sub>O<sub>5</sub> on anatase TiO<sub>2</sub>)

+ The remainder of the products adding up to 100 % by weight were not identified.

These results again demonstrate the excellent activities and selectivities that can be obtained with the catalysts of the invention.



## Claims

1. A process for oxidising hydrocarbons in the gas phase with oxygen or oxygen containing gas consisting of contacting the reaction gases with a catalyst comprising vanadium pentoxide and titanium dioxide, the said catalyst containing 1-50% by weight of vanadium pentoxide and having a BET surface area ranging from 5 to 100 m<sup>2</sup>/g, characterised in that the titanium dioxide is rutile titanium dioxide.
2. The process of claim 1 where the hydrocarbon is a butene or a hydrocarbon mixture containing a butene.
3. The process of claim 1 where the hydrocarbon is o-xylene.
4. Catalyst comprising vanadium pentoxide and titanium dioxide, the said catalyst containing 1-50% by weight of vanadium pentoxide and having a BET surface area ranging from 5 to 100 m<sup>2</sup>/g, characterised in that the titanium dioxide is rutile titanium dioxide.

## COMMUNICATION

1. The subject-matter of claims 1 to 4 is not novel. See document (DI) which describes the processes and the catalyst of present claims 1, 3 and 4 (cf. DI, examples 1-4). See document (DII) which also discloses the subject-matter of present claim 2 (cf. DII, example 3).
2. If you wish to maintain the application, you are invited to submit claims which take the aforementioned objections into account and comply with the requirements of the EPC, especially with regard to novelty, inventive step, clarity, disclosure in the application documents as originally filed and, if necessary, unity (Art. 54 (1) and (2), 56, 84, 123(2) and 82 EPC).
3. In your reply, you should also identify the difference between the new claims and the state of the art and its significance, and present the invention in such a way that both the technical problem to be solved vis-à-vis the state of the art and the solution found (see Rule 27(1)(c) EPC and Guidelines C-IV, 9.5), as well as your position on the question of inventive step, can be understood.
4. According to the Guidelines (C-III, 4.4) an independent claim should specify clearly all the essential features needed to define the invention, i.e. each independent claim must indicate all the features necessary to solve the problem on which the invention is based.
5. Your attention is drawn to the fact that the application may not be amended in such a way that its subject-matter extends beyond the content of the application as filed (Art. 123 (2) EPC). Therefore, and also in view of the Guidelines E-II, 1 and C-VI, 5.4, you should explain from where in the original application documents the new features in any newly formulated claims have been directly and unambiguously derived.
6. It is suggested not to file an adapted description until the Examining Division has indicated that the amended claims are allowable.

**DOCUMENT DI (State of the Art)**

This invention relates to a catalyst containing  $\text{TiO}_2$  and  $\text{V}_2\text{O}_5$  and to an oxidation process in which said catalyst is employed. This catalyst is preferably used in the oxidation of o-xylene or of naphthalene to yield phthalic anhydride or in the oxidation of butenes (such as n-butene) to yield acetic and/or maleic acid.

5

The present catalyst contains 5 to 50 weight % of vanadium pentoxide. It preferably has a BET surface area of 10 to 100  $\text{m}^2/\text{g}$ .

The catalyst may be produced by impregnating a rutile support with an aqueous solution of a thermally decomposable V(IV)-compound. The impregnated support may then be dried and calcined in an oxidising atmosphere to yield the desired catalyst.

Alternatively, a vanadium containing thermally decomposable gaseous compound may be adsorbed onto a rutile support. The support with the vanadium compound adsorbed there upon may then undergo thermal and, if necessary, hydrolysis in order to convert the vanadium compound into vanadium pentoxide.

Finally, the catalyst may be produced by combining a freshly produced  $\text{TiO}_2$  hydrogel with a thermally decomposable V-(IV)-compound (such as vanadium (IV) oxalate), eliminating the solvent (drying step) and calcining the dry mixture. At least one of the drying and calcining steps should be carried out in an oxidising atmosphere, so that vanadium pentoxide is formed.

It is preferred that at least 50 % by weight, preferably at least 90 % by weight of the  $\text{TiO}_2$  in the catalyst is in the rutile form.

25

Preferred methods of making the catalyst of the present invention are illustrated by the following examples 1 and 2.

Example 1

- 5 (a) To 300 g of a stirred 10% aqueous solution of titanium sulphate, 340 g of 15% aqueous ammonia was added in the course of 10 minutes at a temperature of 40 °C. The resulting hydrogel of titanium oxide was filtered, and this precipitate was washed 3 times with water. The precipitate was dried for 3 hours at 110 °C and subsequently for 18 hours at 250 °C.
- 10 (b) 40 g of vanadium pentoxide was suspended in 80 g of pure water, and heated with stirring to 80 °C. Then 84 g of oxalic acid was gradually added to reduce the vanadium and form a vanadium (IV) oxalate solution. When all the oxalic acid was added, the formation of a homogeneous solution confirmed the complete reduction of the vanadium. The solution was then cooled to 40 °C. The hydrogel of titanium oxide obtained in step (a) was added with thorough stirring to the resulting vanadyl oxalate solution, and the mixture was spray dried. The fine spherical particles so spray dried were calcined in a muffle furnace at 350 °C for 3 hours.

5 The resulting catalyst contained titanium oxide in the rutile form (92 %) and the fraction of vanadium in the catalyst was 20.3%, expressed as % by weight of  $V_2O_5$ .

Example 2

- ) A rutile titanium dioxide which had been calcined at 950 °C and had a BET surface area of 10 m<sup>2</sup>/g and was sieved to a particle size range of 200 to 300 micrometers was selected for use as the substrate.
- 25 The catalyst substrate was then placed in a glass tube and a water vapour/air mixture was passed through the tube for two hours at 50 °C and 20 cm<sup>3</sup> per minute. Dry air at 145 °C was then passed through the tube for a further four hours to remove excess water from the catalyst substrate. The tube was then allowed to cool to room temperature and dry air containing vanadium oxytrichloride ( $VOCl_3$ ) vapour was passed through the tube overnight.

Subsequently the temperature of the tube was then raised slowly to 350 °C during which air was passed through the tube to remove hydrogen chloride gas and to complete the conversion of vanadium oxytrichloride to vanadium pentoxide.

- 5 This treatment of the rutile support was repeated 5 times in order to increase the amount of vanadium adsorbed on the support.

The amount of vanadium pentoxide associated with the titanium dioxide was found to be 21,7 % by weight  $V_2O_5$ . Ninety six % of the  $TiO_2$  was in the rutile form.

10

### Example 3

The catalysts prepared by the procedure reported in examples 1 and 2 were used for the fluidised bed gas-phase oxidation with air of naphthalene to phthalic anhydride.

The process was run at 330 °C in a fluidised bed of the catalyst. Liquid naphthalene was injected directly at the bottom of the catalyst bed and evaporated immediately; air was fed in via a distributor plate.

Naphthalene conversions of over 90 % were observed. A commercial platinum on silica catalyst was only able to provide 40 % conversion under these conditions.

### Example 4

- 25 The catalysts prepared by the procedure reported in examples 1 and 2 were also used for the gas-phase oxidation with air of o-xylene to phthalic anhydride.

The process was run at 305 °C and at hourly space velocities of the gas of about 5,000 hours<sup>-1</sup>; the o-xylene conversion was almost 100 %.

**DOCUMENT DII (State of the Art)**

The present invention relates to a new process for making catalysts based on rutile ( $\text{TiO}_2$ ) and  $\text{V}_2\text{O}_5$ . The present catalysts are, e.g., useful in the oxidation of o-xylene or naphthalene to yield phthalic anhydride or in the oxidation of butenes to yield acetic and/or maleic acids.

- 5 This new process ensures a more even distribution of the  $\text{V}_2\text{O}_5$  within the  $\text{TiO}_2$ . The new process differs from the ones described in the prior art in that vanadium and titanium oxides are coprecipitated in an aqueous solution.

This process preferably comprises the following stages:

- ) (i) preparation of an aqueous solution of a Ti(IV) compound,  
(ii) preparation of an aqueous solution of a V(IV) compound  
(iii) mixing solutions (i) and (ii),  
(iv) coprecipitation of vanadium and titanium oxides, and  
(v) separation of the precipitate obtained in (iv), drying and calcining the precipitate.

5 Step (i) is most easily effected by partial hydrolysis of  $\text{TiCl}_4$  to obtain an aqueous solution at a final pH below 1.0.

Step (ii) may be carried out by dissolving solid  $\text{V}_2\text{O}_5$  in an aqueous oxalic acid solution.

) The coprecipitation (step (iv) ) is preferably carried out by adding a base to the combined solution or by heating this solution at an appropriate pH-value.

25 Calcination requires temperatures above 250 °C. The drying and/or calcination in step (v) should be carried out in an oxidative medium in order to effect the conversion of the vanadium oxide to  $\text{V}_2\text{O}_5$ .

The invention is further illustrated by the following examples.

Example 1

- 5 (a) 5 g of  $V_2O_5$  (vanadium pentoxide) were suspended in a solution of oxalic acid (10.4 g in  $100\text{ cm}^3$  of distilled  $H_2O$ ) in a three-necked flask; the suspension was heated, with stirring and under a nitrogen stream, to  $70\text{ }^\circ\text{C}$ , until the  $V_2O_5$  had been completely reduced to V(IV), that is to say until a clear blue solution was obtained. The time needed for complete reduction was about 2 hours. The solution was cooled and any unreacted residues of  $V_2O_5$  were separated off by filtration.
- 10 (b)  $25\text{ cm}^3$  of  $TiCl_4$  were slowly added dropwise to a second flask immersed in a water/ice bath and containing a solution of HCl in  $H_2O$  ( $5\text{ cm}^3$  of 37% HCl in  $150\text{ cm}^3$  of  $H_2O$ ); the solution was kept under vigorous stirring during the partial hydrolysis of the  $TiCl_4$ .

The two solutions were then mixed whilst cold.

The precipitation was carried out by adding dropwise, with stirring, a solution of  $NH_4OH$  (30% of  $NH_3$ ) until pH 1.0 was obtained in the solution. An initial opalescence formed, and the precipitation was complete after about 12 hours.

The precipitate was dried at  $80\text{ }^\circ\text{C}$  for 24 hours and calcined at  $350\text{ }^\circ\text{C}$  for 3 hours. The BET-surface area of the catalyst obtained was  $45\text{ m}^2/\text{g}$ . The  $TiO_2$  obtained was in the rutile crystal form, and the fraction of vanadium in the catalyst is 21.8%, expressed as % by weight of  $V_2O_5$ .

Examples 2 and 3

25

The catalyst produced according to example 1 was tested

- 30 - in the gas phase oxidation of o-xylene to yield phthalic anhydride at temperatures ranging from  $290$  to  $310\text{ }^\circ\text{C}$  and at hourly space velocities of the order of  $5,000\text{ hours}^{-1}$ ; almost quantitative o-xylene conversions were observed;
- in the oxidation of n-butene. The reaction was carried out in a fluidised bed reactor (15l/h of air; 1 l/h of n-butene, 10 l/h of steam; reaction temperature:  $310\text{ }^\circ\text{C}$ ). High yields of acetic acid were observed whilst oxidation to oxides of carbon was kept to a minimum.