

ALCOHOLS OR KETONES BY HETEROGENEOUS CATALYSIS

The present invention relates to the oxidation of hydrocarbons, alcohols or ketones, in the liquid phase and in the presence of a heterogeneous catalyst.

The invention relates more particularly to an oxidation process leading to the at least partial production of acids from saturated or unsaturated hydrocarbons, alcohols or ketones.

The oxidation of hydrocarbons into corresponding acids in the presence of a homogeneous catalyst, that is to say one which is dissolved in the reaction medium, is well known. Thus, American patent US-A-2,223,493, published in December 1940, describes the oxidation of cyclic hydrocarbons into corresponding diacids, in a liquid phase generally containing acetic acid, at a temperature of at least 60°C, using a gas containing oxygen and in the presence of a homogeneous oxidation catalyst such as a cobalt compound.

However, processes using homogeneous-phase catalysts have the drawback, at the end of the reaction, of requiring the separation of the dissolved catalyst, which is generally to be recycled, from the reaction products which must be purified.

Patent EP-A-0,519,569 describes the catalytic oxidation of hydrocarbons, such as alkanes or

cycloalkanes, with molecular oxygen, in the liquid phase and in the presence of a heterogeneous catalyst consisting of a molecular sieve containing cobalt implanted in the crystal lattice as active metal. The catalyst may be separated, for example by filtration or centrifugation, and may if necessary be recycled. The example of this patent, performed with cyclohexane in the presence of acetic acid, shows that cyclohexyl acetate and cyclohexanone are essentially obtained.

International Application WO 94/17021 describes a process for the catalytic autoxidation of various hydrocarbons or alcohols derived from these hydrocarbons, by reaction of oxygen, in the liquid phase, at high temperature and in the presence of a molecular sieve containing aluminium oxide, silicon oxide and/or phosphorus oxide and a metal, incorporated in the crystal lattice, chosen from the metals of groups 4, 5, 6, 7 and 8 of the Periodic Table and rare-earth metals. The examples performed with these heterogeneous catalysts containing chromium or manganese show that the alcohol and the ketone corresponding to the hydrocarbon employed or the ketone corresponding to the alcohol employed are obtained.

The processes described in the above two patent applications show the possibility of heterogeneous catalysis in the oxidation of hydrocarbons into alcohols and ketones. However, an essential interest of the oxidation of hydrocarbons is

the direct production of corresponding acids or diacids, in particular such as the production of adipic acid by oxidation of cyclohexane.

The subject of the present invention is, precisely, a process for the oxidation of hydrocarbons, alcohols or ketones by molecular oxygen, using heterogeneous catalysis and leading at least partially to the corresponding acids or diacids.

More precisely, the invention consists of a process for the oxidation into carboxylic acid, by molecular oxygen or a gas containing the same, of a hydrocarbon, an alcohol or a ketone, in the liquid phase, in an at least partial solvent of the intended carboxylic acid, in the presence of a heterogeneous catalyst containing at least manganese atoms incorporated in the crystal matrix of a molecular sieve.

The hydrocarbons which are used as starting materials in the process of the invention are more particularly alkanes, cycloalkanes, alkylaromatic hydrocarbons, alkenes and cycloalkenes having from 3 to 20 carbon atoms.

The alcohols or ketones which are also used as substrates are those which correspond to the hydrocarbons defined above.

Among these hydrocarbons, one of the most advantageous is most definitely cyclohexane, the oxidation of which leads to adipic acid, one of the

basic compounds of nylon 6-6.

In a similar manner and for the same reason, cyclohexanol and cyclohexanone are among the most advantageous alcohols and ketones which may be used in the present oxidation process.

The molecular sieves in whose crystal lattice the manganese is incorporated are, in particular, metasilicates (also called zeolites) such as aluminosilicates, borosilicates, ferrosilicates and gallosilicates, silicoaluminophosphates (SAPOs), aluminophosphates (APOs) and silicalites.

Metasilicates are crystallized tectosilicates of natural or synthetic origin whose crystals result from the three-dimensional assembly of tetrahedral units of SiO_4 and TO_4 , T representing a trivalent element such as aluminium, gallium, boron or iron, preferably aluminium. The metasilicates of aluminosilicate type are the most common.

The metasilicates have, within the crystal lattice, a system of cavities connected together by channels of well-defined diameter which are referred to as pores.

The metasilicates may exhibit a one-dimensional, two-dimensional or three-dimensional lattice.

Among the metasilicates which may be used are natural zeolites such as, for example, offretite, clinoptilolite, erionite, chabazite and phillipsite.

Synthetic metallosilicates are also entirely suitable.

Examples of synthetic metallosilicates with a one-dimensional lattice which may be mentioned, inter alia, are zeolite ZSM-4, zeolite L, zeolite ZSM-12, zeolite ZSM-22, zeolite ZSM-23, and zeolite ZSM-48.

As examples of metallosilicates with a two-dimensional lattice which may preferably be used, mention may be made of beta zeolite, mordenite and ferrierite.

As regards the metallosilicates with a three-dimensional lattice, mention may be made more particularly of zeolite Y, zeolite X, zeolite ZSM-5, zeolite ZSM-11 and offretite.

Use is preferably made of synthetic metallosilicates and more particularly of those which are in the following forms:

- mazzite with an Si/Al molar ratio of 3.4
- zeolite L with an Si/Al molar ratio of 1.5 to 3.5
- mordenite with an Si/Al molar ratio of 5 to 15
- ferrierite with an Si/Al molar ratio of 3 to 10
- offretite with an Si/Al molar ratio of 4 to 8.5
- beta zeolites with an Si/Al molar ratio of 15 to 25

- zeolites Y, in particular the zeolites obtained after de-alumination treatment, more particularly zeolites US-Y with an Si/Al molar ratio of greater than 3, preferably of between 6 and 60

- zeolite X of faujasite type with an Si/Al molar ratio of 0.7 to 1.5

- zeolites ZSM-5 or aluminium silicate with an Si/Al molar ratio of 10 to 2000

- zeolite ZSM-11 with a molar ratio of 5 to 30.

The metasilicates used in the present process are known products described in the literature [cf Atlas of zeolites structure types by W. M. Meier and D. H. Olson, published by the Structure Commission of the International Zeolite Association (1978)]. Use may be made of commercially available zeolites or they may be synthesized according to processes described in the literature.

Among the silicalites, silicalite of type 1 of similar structure to ZSM-5, silicalite of type 2 of similar structure to ZSM-11 and beta silicalite are used more particularly.

The amount of manganese incorporated into the molecular sieves may vary widely and will be determined during the preparation of the heterogeneous catalysts.

It may be indicated that, generally, the manganese represents by weight from 0.1% to 10% of the total

weight of the molecular sieve, without these limit values being absolute. However, contents which are excessively low needlessly dilute the active part of the catalyst, whereas contents which are too large run the risk of causing partial dissolution of the manganese, when the catalyst is used.

The amount of heterogeneous catalyst employed may be extremely variable, in particular as a function of the conditions for carrying out the process: process in continuous, batchwise or semi-continuous operation. In general, the amount of catalyst, expressed as a weight percentage of manganese metal relative to the substrate to be oxidized, represents from 0.001% to 5%.

Within the context of continuous operation of the process, it is quite obvious that the amount of catalyst relative to the substrate is unimportant and that the ratios indicated above may thus be much larger.

Besides manganese, the heterogeneous catalysts used may also contain one or more other elements which may play a catalytic role. These elements will be chosen in particular from the elements of groups 4a, 5a, 6a, 7a, 8 and 4b of the Periodic Table of the elements as published in Bulletin de la Société Chimique, No. 1 of January 1966, as well as the group of yttrium and rare-earth metals.

As an illustration of such elements which may be present with the manganese, mention may be made of

titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, tungsten, molybdenum, rhenium, cobalt, nickel, iron, ruthenium, germanium, tin and cerium. The content of these elements, expressed by weight relative to the weight of the substrate to be oxidized, is generally between 0.001% and 5%.

The temperature at which the oxidation reaction is performed is very variable, in particular depending on the substrate used. It is generally between 50°C and 200°C and preferably between 80°C and 140°C.

The pressure is not a critical parameter of the process. It may be less than, equal to or greater than atmospheric pressure. It will generally be between 0.1 MPa (1 bar) and 20 MPa (200 bar), without these values being imperative.

Pure oxygen, air, air enriched with or depleted in oxygen or alternatively oxygen diluted with an inert gas may be used.

The liquid reaction medium contains an at least partial solvent for the carboxylic acid whose preparation is intended by the use of the process of the invention. This solvent may be very varied in nature insofar as it is not substantially oxidizable under the reaction conditions. It may be chosen in particular from polar protic solvents and polar aprotic solvents. Polar protic solvents which may be mentioned, for example, are carboxylic acids containing only

primary or secondary hydrogen atoms, in particular aliphatic acids having from 1 to 9 carbon atoms, perfluoroalkylcarboxylic acids such as fluoroacetic acid, water and alcohols when the catalyst used is
5 derived from a zeolite or from a silicalite. Polar aprotic solvents which may be mentioned, for example, are lower alkyl esters (= alkyl radical having from 1 to 4 carbon atoms) of carboxylic acids, in particular aliphatic carboxylic acids having from 1 to 9 carbon
10 atoms or perfluoroalkylcarboxylic acids, and tetramethylenesulphone (or sulpholane).

Acetic acid is generally preferred, in particular when the substrate to be oxidized is cyclohexane.

15 The solvent, as defined above, represents from 1% to 99% of the weight of the reaction medium, preferably from 10% to 90% and, even more preferably, from 20% to 80%.

The liquid reaction medium consists of the
20 substrate to be oxidized, solvent and heterogeneous catalyst; it may also contain, where appropriate, other compounds, in particular such as initiators. The initiators are often hydroperoxides such as, for example, cyclohexyl hydroperoxide or tert-butyl
25 hydroperoxide. They are also ketones or aldehydes such as, for example, cyclohexanone, which is one of the compounds formed during the oxidation of cyclohexane or acetaldehyde. The initiator preferably represents from

0% to 20% by weight relative to the weight of the reaction mixture used, without these proportions having a critical value, in particular when the process is formed continuously. The initiator is especially useful
5 when starting the oxidation and, in particular, when the reaction is performed at a temperature below 120°C. It may be introduced from the start of the reaction.

A strong acid, that is to say in the present invention an inorganic or organic acid whose pKa is
10 less than or equal to 3, may also be added to the reaction mixture as defined above. Non-limiting examples of such acids which may be mentioned are nitric acid and trifluoroacetic acid. The addition of such a strong acid has the effect of improving the
15 reaction kinetics and generally also its selectivity towards carboxylic acid. The strong acid represents from 0% to 20% by weight relative to the weight of the reaction mixture.

The heterogeneous catalyst is prepared
20 according to known techniques, which a person skilled in the art is capable of adapting, as a function of the amount of manganese and of the nature and amounts of the other elements to be incorporated into the crystal matrix of the molecular sieve. Reference may be made,
25 for example, to the process described in US patents 4,759,919, 4,567,029 and 4,310,440 for the preparation of aluminophosphates, and in US 4,410,501 for the preparation of manganese silicalites.

In general, the compounds of the various elements entering into the crystal lattice, that is to say a source of silicon, phosphorus, aluminium or boron or gallium or iron, manganese and other possible elements to be incorporated into the crystal lattice of the molecular sieve, are mixed in the desired proportions, along with a structuring agent and a mobilizing agent, and the mixture obtained is subjected to a hydrothermal treatment, in order to obtain the zeolite, the silicalite, the aluminophosphate or the silicoaluminophosphate. The structuring agent is, for example, an amine such as diethanolamine, methylamine or hexamethylenediamine or a quaternary ammonium salt. The mobilizing agent may be, in particular, a hydroxide, a fluoride or an amine. The temperature of the hydrothermal treatment of the mixture is between about 100°C and about 200°C, preferably between 120°C and 170°C and, even more preferably, between 125°C and 150°C. At the end of the hydrothermal treatment, the material obtained is separated according to the standard techniques of solid/liquid separation, preferably by filtration. It may be advantageous to carry out a washing operation, preferably with water.

The material obtained is subjected to a drying at a temperature chosen preferably between 50°C and 120°C, under atmospheric pressure or under reduced pressure chosen between 133 Pa and atmospheric pressure.

Lastly, the material obtained is calcined in air, at a temperature of between 300°C and 500°C, preferably of between 400°C and 500°C.

The final catalyst may be used as a powder or
5 may be placed, for example, in the shape of beads, pastilles, extrudates or crushed particles, according to various known techniques.

The catalyst may also be placed in shape using, in a conventional manner, a binder of silica,
10 alumina or clay type.

As indicated above, the process of the invention may be carried out in a batchwise, semi-continuous or continuous manner. Heterogeneous catalysis lends itself particularly well to a
15 continuous or semi-continuous operation of the process.

The examples which follow illustrate the invention.

EXAMPLE 1

1) - Preparation of the catalyst
20 (procedure similar to that of Example 88 of US 4,567,029)

A solution of 8.2 g of manganese acetate $[\text{Mn}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}]$ in 107.4 g of water is added to 46.9 g of aluminium isopropoxide. To the gel thus
25 formed are added a solution composed of 46.2 g of 85% phosphoric acid, 46.3 g of water and 46.9 g of diethanolamine.

The reaction mixture is heated under

autogenous pressure for 24 h at 200°C. The solid is recovered by filtration, washed with water and then air-dried at room temperature and, lastly, calcined to a temperature of 550°C.

5 An Mn aluminophosphate having a content of 5.7% by weight of Mn is thus obtained.

2) - Oxidation of cyclohexane

The following are loaded into a 30 ml Pyrex glass bulb:

- 10 - 60 mmol of cyclohexane
 - 5.8 g of acetic acid
 - 0.03 g of acetaldehyde
 - 0.1 g (0.1 mmol of Mn) of Mn aluminophosphate prepared in 1).

15 The bulb is placed in a 125 ml autoclave fitted with means of heating, of introducing gas, of regulating the pressure and of stirring.

The mixture is heated with stirring and under a static air pressure of 100 bar, at 105°C and is
20 maintained at this temperature for 3 h.

After cooling, the catalyst is separated out by filtration. A liquid two-phase mixture is obtained, which is separated by settling of the phases into a cyclohexane layer and an acetic layer.

25 The two layers are assayed by gas chromatography.

The following results are obtained:

- degree of conversion (DC) of the

- cyclohexane: 6.1 %
- yield (CY) of cyclohexanol + cyclohexanone
+ adipic acid relative to the cyclohexane
converted: 90.2%
- 5 - CY of adipic acid relative to the
cyclohexane converted: 57.4%
- adipic acid/total of the diacids formed
molar ratio: 90.9%
- Mn passed into solution: <1% of the total
10 Mn employed.

EXAMPLE 2

1) - Preparation of the catalyst

Two solutions A and B are prepared in the
following manner.

- 15 Solution A : 0.716 g of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ is
dissolved in 40 g of water.

- Solution B : 9.53 g of tetrapropylammonium
bromide are dissolved in 43 g of water, which have been
premixed with 22.14 g of aqueous methylamine solution
20 (at a concentration of 40% by weight).

Solution A is added to solution B with
stirring at room temperature, over 15 minutes.

- 7.89 g of silica (sold under the trade name
Aerosil 50) are then added slowly, with vigorous
25 stirring, to the mixture obtained above. The resulting
gel is placed in a teflon jacketed autoclave and is
treated at 60°C for 1 h 30 and then at 185°C for 120 h
without stirring. The Mn silicalite obtained is

separated from the gel by centrifugation, washed with demineralized water until a neutral pH is obtained, dried and then calcined in air to a temperature of 550°C.

5 An Mn silicalite having a content of 2% by weight of Mn is thus obtained.

2) - Oxidation of cyclohexane

Example 1 is repeated (under the same operating conditions and in the same equipment), with
10 the following charges:

- 60 mmol of cyclohexane
- 5.8 g of acetic acid
- 0.03 g of acetaldehyde
- 0.54 g (0.2 mmol of Mn) of Mn catalyst
15 prepared in 1).

By assaying the two layers by gas chromatography, the following results are obtained:

- degree of conversion (DC) of the cyclohexane: 7 %
- 20 - yield (CY) of cyclohexanol + cyclohexanone + adipic acid relative to the cyclohexane converted: 81 %
- CY of adipic acid relative to the cyclohexane converted: 39 %
- 25 - Mn passed into solution: <1% of the total Mn employed.

COMPARATIVE TEST1) - Preparation of the catalyst

Catalyst: manganese zeolite synthesized according to Example 1 of US patent 4,491,637, substituting the cobalt nitrate with manganese nitrate.

140 g of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ are dissolved in 100 g of water and this solution is added to 500 g of zeolite HY. The aqueous phase is evaporated with a rotary evaporator under reduced pressure (10 mbar) and at a temperature of 80°C - 90°C. This procedure is carried out until the catalyst is dry. It is then calcined for 3 hours at 550°C.

The catalyst contains 5.3% of manganese.

2) - Oxidation of cyclohexane

Example 1 is repeated (under the same operating conditions and in the same equipment) with the following charges:

- 60 mmol of cyclohexane
- 5.8 g of acetic acid
- 0.03 g of acetaldehyde
- 0.1 g (0.097 mmol of Mn) of Mn catalyst prepared in 1).

By assaying the two layers by gas chromatography, the following results are obtained:

- degree of conversion (DC) of the cyclohexane: 1.5 %
- yield (CY) of cyclohexanol + cyclohexanone relative to the cyclohexane

converted: 100%

- CY of adipic acid relative to the

cyclohexane converted: 0%

- Mn passed into solution: 13% of the total

5 Mn employed.

COMPARATIVE TEST B

Oxidation of cyclohexane under homogeneous catalysis with cobalt acetate

Example 1 is repeated (under the same
10 operating conditions and in the same equipment) with
the following charges:

- 60 mmol of cyclohexane
- 5.8 g of acetic acid
- 0.03 g of acetaldehyde
- 15 - 0.0174 g (0.07 mmol of Co) of cobalt
acetate tetrahydrate.

After cooling, a two-phase liquid mixture is
obtained.

By assaying the two layers by gas
20 chromatography, the following results are obtained:

- degree of conversion (DC) of the
cyclohexane 10.1%
- yield (CY) of cyclohexanol +
cyclohexanone relative to the
- 25 cyclohexane converted: 84.7%
- CY of adipic acid relative to the
cyclohexane converted: 53.2%
- adipic acid/total of the diacids formed

molar ratio: 84.7%

COMPARATIVE TEST C

Oxidation of cyclohexane under homogeneous catalysis with manganese acetate

5 Example 1 is repeated (under the same
operating conditions and in the same equipment) with
the following charges:

- 60 mmol of cyclohexane
- 5.8 g of acetic acid
- 10 - 0.03 g of acetaldehyde
- 0.0172 g (0.07 mmol of Mn) of manganese
acetate tetrahydrate.

After cooling, a single homogeneous phase is
obtained.

15 By assaying this layer by gas chromatography,
the following results are obtained:

- degree of conversion (DC) of the
cyclohexane: 0.2%
- yield (CY) of cyclohexanol +
20 cyclohexanone relative to the
cyclohexane converted: 100%
- CY of adipic acid relative to the
cyclohexane converted: 0%

EXAMPLE 3

25 1) - Preparation of the catalyst
(procedure similar to that of Example 88 of
US 4,567,029)

Working as in Example 1, but with charges

other than Mn acetate, an Mn aluminophosphate having an Mn content of 3% by weight is prepared.

2) Oxidation of cyclohexane

This example was carried out in a 250 ml Parr reactor equipped with a condenser. A flow-meter and oxygen analyser system allows the gas flow rate at the reactor inlet and outlet to be checked at any moment, as well as the oxygen content (and consequently the rate of consumption of oxygen).

In addition, the reactor is fitted with heating and pressure-regulating means and a stirrer.

The following are loaded into the reactor:

- 58 g of cyclohexane (690 mmol)
- 70 g of acetic acid
- 0.24 g of acetaldehyde (5.46 mmol)
- 0.52 g (0.28 mmol of Mn) of the Mn aluminophosphate prepared in 1).

The mixture is heated with stirring (800 revolutions/minute), under pressure of air - containing 10% oxygen - of 20 bar, at 110°C and at a flow rate of 20 litres of air/hour. This temperature is maintained for 3 h.

After cooling, the catalyst is separated out by filtration. A two-phase liquid mixture is obtained, which is separated, by settling, into a cyclohexane layer and an acetic layer.

The two layers are assayed by gas chromatography.

The following results are obtained:

- degree of conversion (DC) of the cyclohexane: 2.2%
- yield (CY) of cyclohexanol + cyclohexanone + adipic acid relative to the cyclohexane converted: 100%
- CY of adipic acid relative to the cyclohexane converted: 11%
- adipic acid/total of the diacids formed molar ratio: 100%

EXAMPLE 4

1) - Preparation of the catalyst

An Mn silicalite is prepared by mixing 1 mol of silica, 0.1 mol of tetrapropylammonium bromide, 1 mol of methylamine, 0.5 mol of hydrogen fluoride, 0.03 mol of manganese acetate tetrahydrate and 40 mol of water.

The mixture is heated for 2 days at 200°C without stirring.

It is filtered, washed with water and then calcined for 3 hours at 500°C.

An Mn silicalite having a content of 1.0% by weight of Mn is obtained.

2) - Oxidation of cyclohexane

Example 1 is repeated (under the same operating conditions and in the same equipment) with the following charges:

- 60 mmol of cyclohexane
 - 5.8 g of acetic acid
 - 0.03 g of acetaldehyde
 - 0.33 g (0.06 mmol of Mn) of the Mn catalyst prepared in 1).
- 5

By assaying the two layers by gas chromatography, the following results are obtained:

- degree of conversion (DC) of the cyclohexane: 8%
- 10 - yield (CY) of cyclohexanol + cyclohexanone + adipic acid relative to the cyclohexane converted: 74%
- CY of adipic acid relative to the cyclohexane converted: 43%
- 15 - adipic acid/total of the diacids formed molar ratio: 76%

CLAIMS

1. Process for the oxidation into carboxylic acid, by molecular oxygen or a gas containing the same, of a hydrocarbon, an alcohol or a ketone, in the liquid phase, in an at least partial solvent of the intended carboxylic acid, in the presence of a heterogeneous catalyst containing at least manganese atoms incorporated in the crystal matrix of a molecular sieve.
2. Process according to Claim 1, characterized in that the hydrocarbons used as starting materials are alkanes, cycloalkanes, alkylaromatic hydrocarbons, alkenes and cycloalkenes having from 3 to 20 carbon atoms and the alcohols or ketones are those which correspond to these hydrocarbons.
3. Process according to Claim 1, characterized in that the hydrocarbon used is cyclohexane.
4. Process according to Claim 1, characterized in that the alcohol used is cyclohexanol and the ketone used is cyclohexanone.
5. Process according to one of Claims 1 to 4, characterized in that the molecular sieves in whose crystal lattice the manganese is incorporated are chosen from metasilicates (zeolites) such as aluminosilicates, borosilicates, ferrosilicates and gallosilicates, silicoaluminophosphates (SAPOs), aluminophosphates (APOs) and silicalites.



6. Process according to one of Claims 1 to 5, characterized in that the manganese represents by weight from 0.1% to 10% of the total weight of the molecular sieve.

5 7. Process according to one of Claims 1 to 6, characterized in that the amount of catalyst, expressed as a weight percentage of manganese metal relative to the substrate to be oxidized, represents from 0.001% to 5%.

10 8. Process according to one of Claims 1 to 7, characterized in that the heterogeneous catalysts used contain one or more other elements chosen from the elements of groups 4a, 5a, 6a, 7a, 8 and 4b of the Periodic Table of the elements, as published in the
15 Bulletin de la Société Chimique, No. 4 of January 1966, as well as of the group of yttrium and rare-earth metals.

9. Process according to Claim 8, characterized in that the heterogeneous catalysts used
20 contain one or more other elements chosen from titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, tungsten, molybdenum, rhenium, cobalt, nickel, iron, ruthenium, germanium, tin and cerium, at a content, expressed by weight relative to
25 the weight of the substrate to be oxidized, of between 0.001% and 5%.

10. Process according to one of Claims 1 to 9, characterized in that the solvent is chosen from



polar protic solvents such as carboxylic acids containing only primary or secondary hydrogen atoms, in particular aliphatic acids having from 1 to 9 carbon atoms, perfluoroalkylcarboxylic acids, water and
5 alcohols when the catalyst used is derived from a zeolite or from a silicalite and polar aprotic solvents such as lower alkyl esters of carboxylic acids, in particular aliphatic carboxylic acids having from 1 to 9 carbon atoms or perfluoroalkylcarboxylic acids, and
10 tetramethylenesulphone (or sulpholane).

11. Process according to one of Claims 1 to 10, characterized in that the temperature at which the oxidation reaction is performed is between 50°C and 200°C and preferably between 80°C and 140°C and the
15 pressure is between 0.1 MPa (1 bar) and 20 MPa (200 bar).

12. Process according to one of Claims 1 to 11, characterized in that the solvent used contains acetic acid.

20 13. Process according to one of Claims 1 to 12, characterized in that the solvent represents from 1% to 99% of the weight of the reaction medium, preferably from 10% to 90% and, more preferably, from 20% to 80%.

IN THE MATTER OF a Singapore
Application corresponding to
PCT Application PCT/FR96/00515

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(57) Abstract

A method for oxidising liquid-phase hydrocarbons, alcohols or ketones in the presence of a heterogeneous catalyst. The method particularly enables the oxidation of a liquid-phase hydrocarbon, alcohol or ketone to carboxylic acid using molecular oxygen or a gas containing same, in an at least partial solvent for the desired carboxylic acid, and in the presence of a heterogeneous catalyst comprising at least manganese atoms incorporated into the crystal lattice of a molecular sieve. The liquid phase comprises a solvent generally selected from polar protic solvents and polar aprotic solvents, and particularly from carboxylic acids and esters thereof.

(57) Abrégé

La présente invention concerne l'oxydation d'hydrocarbures, d'alcools ou de cétones, en phase liquide et en présence d'un catalyseur hétérogène. Il s'agit plus précisément de l'oxydation en acide carboxylique, par l'oxygène moléculaire ou un gaz en contenant, d'un hydrocarbure, d'un alcool ou d'une cétone, en phase liquide, dans un solvant au moins partiel de l'acide carboxylique visé, en présence d'un catalyseur hétérogène comportant au moins des atomes de manganèse incorporés dans le réseau cristallin d'un tamis moléculaire. La phase liquide comporte un solvant généralement choisi parmi les solvants protiques polaires et les solvants aprotiques polaires, plus particulièrement parmi les acides carboxyliques et leurs esters.

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BJ	Benin	MC	Monaco
BR	Brazil	MD	Republic of Moldova
BY	Belarus	MG	Madagascar
CA	Canada	ML	Mali
CF	Central African Republic	MN	Mongolia
CG	Congo	MR	Mauritania
CH	Switzerland	MW	Malawi
CI	Ivory Coast	MX	Mexico
CM	Cameroon	NE	Niger
CN	China	NL	Netherlands
CS	Czechoslovakia	NO	Norway
CZ	Czech Republic	NZ	New Zealand
DE	Germany	PL	Poland
DK	Denmark	PT	Portugal
EE	Estonia	RO	Romania
ES	Spain	RU	Russian Federation
FI	Finland	SD	Sudan
FR	France	SE	Sweden
GA	Gabon	SG	Singapore
GB	United Kingdom	SI	Slovenia
GE	Georgia	SK	Slovakia
GN	Guinea	SN	Senegal
GR	Greece	SZ	Swaziland
HU	Hungary	TD	Chad
IE	Ireland	TG	Togo
IT	Italy	TJ	Tajikistan
JP	Japan	TT	Trinidad and Tobago
KE	Kenya	UA	Ukraine
KG	Kyrghyzstan	UG	Uganda
KP	Democratic People's Republic of Korea	US	United States of America
KR	Republic of Korea	UZ	Uzbekistan
		VN	Vietnam