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PROCESS FOR THE OXIDATION OF HYDROCARBONS, ALCOHOLS
AND/OR KETONES

The present invention relates to the
5 oxidation with oxygen, or a gas containing it, of
hydrocarbons to the corresponding carboxylic acids,
alcohols and/or ketones or of alcohols and/or ketones
to the corresponding carboxylic acids.

The direct oxidation with oxygen of
10 hydrocarbons, more particularly of cycloalkanes, in the
presence of a catalyst, is a process which has been
studied for a long time. The reason for this is that
there would be obvious advantages in avoiding the use
of an oxidizing agent such as nitric acid, used in one
15 of the steps of the current industrial processes, which
would spare the need to process the nitrogen oxides
generated.

In the many variants of such a process of
catalytic oxidation with oxygen, cobalt is the catalyst
20 most frequently recommended.

Thus, American patent US-A-2 223 493,
published in December 1940, describes the oxidation of
cyclic hydrocarbons to the corresponding diacids, in a
liquid phase generally comprising acetic acid, at a
25 temperature of at least 60°C, using a gas containing

oxygen and in the presence of an oxidation catalyst such as a cobalt compound.

American patent US-A-4 902 827, published in February 1990, describes an improvement to the air
5 oxidation of cyclohexane to adipic acid, in a liquid phase comprising acetic acid, at a temperature of from 80°C to 160°C and in the presence of an oxidation catalyst comprising a soluble cobalt compound and a soluble zirconium and/or hafnium compound.

10 More recently, it has been recommended in patent EP-A-0 694 333 to use, in the context of the oxidation of hydrocarbons with oxygen, a catalyst comprising a cobalt salt and a ferric salt.

It has also been recommended in patent
15 EP 0 870 751 to use a catalyst comprising a cobalt salt and a chromium salt to improve the selectivity.

Another common catalyst for this oxidation reaction which may be mentioned is manganese.

For economic reasons but also to make the
20 products obtained easier to purify, it is preferable to work with a catalyst concentration which is as low as possible. Thus, manganese is an advantageous catalyst in processes for oxidizing cyclohexane.

Nevertheless, it turns out that although the
25 selectivities obtained with the catalytic systems used in the prior-art processes described above are acceptable, the production efficiency of these

processes needs to be further improved in order to allow such a reaction to be exploited industrially.

This is what the present invention proposes to achieve. More specifically, an aspect of the present invention consists of a process for oxidizing hydrocarbons, alcohols and/or ketones to carboxylic acid using oxygen or a gas containing it, in a liquid phase in a solvent chosen from polar protic solvents and polar aprotic solvents and in the presence of a catalyst dissolved in the reaction medium, characterized in that the catalyst comprises a soluble manganese and/or cobalt compound, a soluble chromium compound and a soluble iron compound.

The hydrocarbons which are used as starting substrates in the process may be alkanes, cycloalkanes, alkylaromatic hydrocarbons, alkenes and cycloalkenes containing from 3 to 20 carbon atoms.

Among these hydrocarbons, the cycloalkanes, in particular those which have a ring containing from 5 to 12 carbon atoms, are definitely the most important, since their oxidation leads to dicarboxylic acids or to the intermediate cycloalkanols and cycloalkanones.

The hydrocarbon which is most advantageous is cyclohexane, the oxidation of which leads to adipic acid, one of the base compounds of polyamide 6,6, but may also give cyclohexanone leading to caprolactam and thus to polyamide 6.

The present process may also be used for the oxidation of the intermediate alcohols or ketones, in particular cycloalkanols and cyclohexanones containing from 5 to 12 carbon atoms, to prepare the corresponding dicarboxylic acids.

In the text hereinbelow, the process will be described more particularly for the oxidation of hydrocarbons, essentially cycloalkanes, and preferably for the oxidation of cyclohexane.

10 The catalytic system which may comprise manganese and/or cobalt, chromium and iron compounds make it possible to prepare adipic acid directly with good selectivity and improved production efficiency, when the oxidation of cyclohexane is performed. These
15 catalytic properties are obviously very advantageous for an industrial exploitation of this oxidation reaction.

 The catalytic system may comprise either at least one manganese compound which is soluble in the
20 reaction medium, chosen, for example, in a non-limiting manner, from manganese chloride, manganese bromide, manganese nitrate and manganese carboxylates, for instance manganese acetate tetrahydrate, manganese propionate, manganese adipate, manganese glutarate or
25 manganese succinate, or at least one cobalt compound which is soluble in the reaction medium, chosen, for example, in a non-limiting manner, from cobalt

chloride, cobalt bromide, cobalt nitrate and cobalt carboxylates, for instance cobalt acetate tetrahydrate, cobalt propionate, cobalt adipate, cobalt glutarate or cobalt succinate.

- 5 The catalyst also may comprise at least one chromium compound which is soluble in the reaction medium, chosen, for example, in a non-limiting manner, from chromium chloride, chromium bromide, chromium nitrate and chromium carboxylates, for instance
- 10 chromium acetate, chromium propionate, chromium adipate, chromium glutarate or chromium succinate, and mineral or organic chromic acid salts.

- The catalyst also may comprise at least one iron compound which is soluble in the reaction medium,
- 15 chosen, for example, in a non-limiting manner, from iron halides, iron nitrate, iron carboxylates, for instance the acetate, propionate, succinate, glutarate or adipate, and iron chelates, for instance iron acetylacetonates.

- 20 Finally, the catalyst may also comprise at least one zirconium and/or hafnium compound which is soluble in the reaction medium, chosen, for example, in a non-limiting manner, from zirconium chloride, zirconium bromide, zirconium nitrate and zirconium
- 25 carboxylates, for instance zirconium acetate, zirconium propionate, zirconium adipate, zirconium glutarate or zirconium succinate, and hafnium chloride, hafnium

bromide, hafnium nitrate and hafnium carboxylates, for instance hafnium acetate, hafnium propionate, hafnium adipate, hafnium glutarate or hafnium succinate.

The molar ratios between the manganese and/or the cobalt, the chromium and the iron in the catalytic system may vary within a wide range. It is thus possible to use Mn and/or Co/Cr/Fe molar ratios which are advantageously between 1/0.00001/0.0001 and 1/100/100, preferably between 1/0.001/0.01 and 1/10/10.

The amount of zirconium or hafnium, when they are present, may vary in molar ratios, relative to the manganese or cobalt, which are similar to those indicated above for chromium.

The catalyst may be obtained in situ by loading the manganese and/or cobalt, chromium, iron and optionally zirconium or hafnium compounds into the reaction medium. It may also be prepared at the time of use by mixing the said compounds in the proportions required to obtain the desired Mn and/or Co/Cr/Fe and optionally Zr and/or Hf molar ratios. Preferably, this mixture is prepared using a solvent, advantageously a solvent of the same nature as the one used for the oxidation reaction or directly in this solvent.

The amount of catalyst, expressed as a weight percentage of metal elements (manganese, cobalt, chromium, iron and, optionally, zirconium or hafnium) relative to the reaction mixture, is generally between

0.0001% and 5% and advantageously between 0.001% and 2%, without these values being critical. Nevertheless, it is a case of having an activity which is sufficient without, however, using excessively large amounts. The
5 reason for this is that the catalyst will have to be separated from the final reaction medium and recycled.

It is advantageous also to use a compound which initiates the oxidation reaction. The initiators are often hydroperoxides, for example cyclohexyl
10 hydroperoxide or tert-butyl hydroperoxide. They are also ketones or aldehydes, for example cyclohexanone which is one of the compounds formed during the oxidation of cyclohexane or of acetaldehyde. Generally, the initiator represents from 0.01% to 20% by weight
15 relative to the weight of the reaction mixture used, without these proportions having a critical value. The initiator is useful above all when starting the oxidation and when the oxidation of cyclohexane is performed at a temperature below 120°C. It may be
20 introduced from the start of the reaction.

The liquid reaction medium preferably contains a solvent which is at least a partial solvent for the carboxylic acid and/or the alcohol and/or the ketone whose preparation is intended by carrying out
25 the process of the invention. This solvent may be of very varied nature, provided 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 containing from 2 to 9 carbon atoms, perfluoroalkyl carboxylic acids such as trifluoroacetic acid, and alcohols such as tert-butanol. Polar aprotic solvents which may be mentioned, for example, are lower alkyl esters (= alkyl radical containing from 1 to 4 carbon atoms) of carboxylic acids, in particular of aliphatic carboxylic acids containing from 2 to 9 carbon atoms or of perfluoroalkylcarboxylic acids, tetramethylene sulphone (or sulfolane), acetonitrile, halogenated hydrocarbons such as dichloromethane, and ketones such as acetone.

Acetic acid is preferably used as solvent for the oxidation reaction of cyclohexane. It is convenient to use a catalyst whose manganese and chromium constituents are in the form of compounds derived from the carboxylic acid used as solvent, provided that the said compounds are soluble in the reaction medium. Manganese acetate, chromium acetate and iron acetate are thus preferably used, in particular for this reason.

The solvent, as defined above, generally represents from 1% to 99% by weight of the reaction

medium, preferably from 10% to 90% and even more preferably from 20% to 80%.

The oxidation may also be carried out in the presence of water introduced from the initial stage of the process.

The temperature at which the oxidation reaction is carried out is 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, oxygen-enriched air, oxygen-depleted air or oxygen diluted with an inert gas may be used.

The examples which follow illustrate the invention.

EXAMPLE 1

The reagents below are loaded into a 1.5 l titanium autoclave equipped with heating means via a heating collar, cooling means, a turbomixer and means for introducing and removing gas and for pressure regulation, the autoclave being purged beforehand with nitrogen:

- 292.5 g of cyclohexane
- 357 g of acetic acid
- 3.4 g of cyclohexanone
- 4.16 g (16.7 mmol of Co) of cobalt acetate tetrahydrate
- 0.162 g (0.74 mmol of Cr) of chromium acetate dihydrate
- 1.183 g (3.2 mmol of Fe) of iron acetylacetonate
- 0.8 g of water.

After closing the reactor, it is stirred at 1 000 rpm, a nitrogen pressure of 20 bar is created at 20°C and heat is applied. The temperature reaches 105°C in the bulk over 20 min. The nitrogen is replaced with air containing 5% oxygen under a pressure of 20 bar. The normal gas flow rate of the air is 250 l/h. After a brief period of about a few minutes without consumption of oxygen, the temperature rises by a few degrees and oxygen consumption is observed. The oxygen content of the air is gradually increased to a value of 21%. The oxygen content in the gas leaving the reactor remains less than 5%.

After reaction for 76 minutes, 52.8 normal litres of oxygen have been consumed, corresponding to a degree of conversion of the cyclohexane of about 20%.

After stopping the flushing with air and cooling to a temperature of 70°C, the reaction mixture

is analysed to determine the degree of conversion and the selectivity. These analyses are performed by gas chromatography (the term "selectivity" - ST - means the molar ratio, expressed as a percentage of the number of moles metered, of a species relative to the theoretical number of moles of the species calculated from the number of moles of cyclohexane effectively converted).

The following results are obtained:

- Degree of conversion (DC) of the
10 cyclohexane: 20.7 %
- ST of cyclohexanol relative to the
cyclohexane converted: 6.3 %
- ST of cyclohexanone relative to the
cyclohexane converted: 4.9 %
- 15 - ST of adipic acid relative to the
cyclohexane converted: 67.1 %
- ST of adipic acid + cyclohexanone +
cyclohexanol relative to the cyclohexane
converted: 78.3 %
- 20 - Molar ratio of adipic acid/total diacids
formed: 85.9 %

EXAMPLE 2 - COMPARATIVE

Example 1 is repeated in the same apparatus and under the same operating conditions, loading the
25 following reagents:

- 292.5 g of cyclohexane
- 357 g of acetic acid

- 3.4 g of cyclohexanone
- 4.0 (16.2 mmol of Co) of cobalt acetate tetrahydrate
- 0.157 g (0.64 mmol of Cr) of chromium acetate dihydrate
- 0.6 g of water.

The reaction time is 95 minutes instead of 76 minutes in Example 1, for an equivalent degree of conversion.

The following results are obtained:

- Degree of conversion (DC) of the cyclohexane: 21.1 %
- ST of cyclohexanol relative to the cyclohexane converted: 5.1 %
- ST of cyclohexanone relative to the cyclohexane converted: 3.4 %
- ST of adipic acid relative to the cyclohexane converted: 70.9 %
- ST of adipic acid + cyclohexanone + cyclohexanol relative to the cyclohexane converted: 79.4 %
- Molar ratio of adipic acid/total diacids formed: 85.7 %

This test clearly shows the influence of the iron on the activity of the catalyst. Specifically, in order to obtain a similar degree of conversion of the cyclohexane, the reaction time was 25% shorter in

Example 1, while maintaining an equivalent selectivity towards adipic acid.

EXAMPLE 3 - COMPARATIVE

Example 1 is repeated in the same apparatus
5 and under the same operating conditions, loading the following reagents:

- 292.5 g of cyclohexane
- 357 g of acetic acid
- 3.4 g of cyclohexanone
- 10 - 4.17 g (16.7 mmol of Co) of cobalt acetate tetrahydrate
- 0.8 g of water.

The reaction time is 75 minutes.

The following results are obtained:

- | | | |
|----|---|--------|
| 15 | - Degree of conversion (DC) of the cyclohexane: | 20.3 % |
| | - ST of cyclohexanol relative to the cyclohexane converted: | 11.6 % |
| | - ST of cyclohexanone relative to the cyclohexane converted: | 4.5 % |
| 20 | - ST of adipic acid relative to the cyclohexane converted: | 61.9 % |
| | - ST of adipic acid + cyclohexanone + cyclohexanol relative to the cyclohexane converted: | 78.2 % |
| 25 | - Molar ratio of adipic acid/total diacids formed: | 85.4 % |

This test shows, in comparison with Example 1, the positive effect of the presence of iron and chromium on the selectivity and production efficiency of the catalyst.

5 EXAMPLE 4

Example 1 is repeated in the same apparatus and under the same operating conditions, but loading the following compounds into the reactor:

- 292.5 g of cyclohexane
- 10 - 357 g of acetic acid
- 3.4 g of cyclohexanone
- 4.13 g (16.6 mmol of Co) of cobalt acetate tetrahydrate
- 0.2325 g (1.06 mmol of Cr) of chromium
- 15 acetate dihydrate
- 1.086 g (3.1 mmol of Fe) of iron acetylacetonate
- 0.8 g of water.

The reaction time is 73 minutes.

20 The following results are obtained:

- Degree of conversion (DC) of the cyclohexane: 20.3 %
- ST of cyclohexanol relative to the cyclohexane converted: 9.8 %
- 25 - ST of cyclohexanone relative to the cyclohexane converted: 2.5 %

- ST of adipic acid relative to the cyclohexane converted: 68.8 %
- ST of adipic acid + cyclohexanone + cyclohexanol relative to the cyclohexane converted: 78.3 %
- Molar ratio of adipic acid/total diacids formed: 85.3 %

EXAMPLE 5 - COMPARATIVE

Example 1 is repeated in the same apparatus and under the same operating conditions, but loading the following compounds into the reactor:

- 292.5 g of cyclohexane
- 357 g of acetic acid
- 3.4 g of cyclohexanone
- 4.0 g (16.1 mmol of Co) of cobalt acetate tetrahydrate
- 0.309 g (1.25 mmol of Cr) of chromium acetate dihydrate
- 0.6 g of water.

The reaction induction time is 50 minutes and the reaction time is 160 minutes.

The following results are obtained:

- Degree of conversion (DC) of the cyclohexane: 17 %
- ST of cyclohexanol relative to the cyclohexane converted: 4.6 %

- ST of cyclohexanone relative to the cyclohexane converted: 1.7 %
- ST of adipic acid relative to the cyclohexane converted: 74.3 %
- 5 - ST of adipic acid + cyclohexanone + cyclohexanol relative to the cyclohexane converted: 77.2 %
- Molar ratio of adipic acid/total diacids formed: 83.4 %

10 This test taken in comparison with Example 4 clearly shows the positive effect on the production efficiency of the combination of iron with chromium, without significantly affecting the selectivity.

EXAMPLE 6

15 The reagents below are loaded into a 1.5 l titanium autoclave equipped with heating means via a heating collar, cooling means, a turbomixer and means for introducing and removing gas and for pressure regulation, the autoclave being purged beforehand with
20 nitrogen:

- 292.5 g of cyclohexane
- 357 g of acetic acid
- 3.67 g of cyclohexanone
- 4.13 g (16.6 mmol of Co) of cobalt acetate tetrahydrate
- 25 - 0.1595 g (0.73 mmol of Cr) of chromium acetate dihydrate

- 1.0895 g (3.1 mmol of Fe) of iron acetylacetonate
- 0.8 g of water.

After closing the reactor, it is stirred at
5 1 000 rpm, a nitrogen pressure of 20 bar is created at
20°C and heat is applied. The temperature reaches 105°C
in the bulk over 20 min. The nitrogen is replaced with
air containing 5% oxygen under a pressure of 20 bar.
The normal gas flow rate of the air is 250 l/h. After a
10 brief period of about a few minutes without consumption
of oxygen, the temperature rises by a few degrees and
oxygen consumption is observed. The oxygen content of
the air is gradually increased to a value of 21%. The
oxygen content in the gas leaving the reactor remains
15 less than 5%.

When 50 normal litres of oxygen have been
consumed, corresponding to a degree of conversion of
the cyclohexane of about 20%, continuous injection into
the liquid phase of a solution of acetic acid
20 containing 1.1% by weight of cobalt acetate
tetrahydrate, 0.043% by weight of chromium acetate
dihydrate and 0.3% by weight of iron acetylacetonate at
a flow rate of 3.9 ml/min and an injection of
4.3 ml/min of cyclohexane are begun.

25 The consumption of oxygen during the
injection period is 0.6 l/min.

After stopping the flushing with air and stopping the injections of the reagents, the mixture is cooled to a temperature of 70°C. The reaction mixture is analysed to determine the various degrees of conversion and selectivity. These analyses are performed by gas chromatography.

The following results are obtained:

	- Degree of conversion (DC) of the cyclohexane:	19.6 %
10	- ST of cyclohexanol relative to the cyclohexane converted:	6.5 %
	- ST of cyclohexanone relative to the cyclohexane converted:	6.0 %
15	- ST of adipic acid relative to the cyclohexane converted:	65.3 %
	- ST of adipic acid + cyclohexanone + cyclohexanol relative to the cyclohexane converted:	77.8 %
20	- Molar ratio of adipic acid/total diacids formed:	85.1 %

The production efficiency of the catalyst is 60.7 g of adipic acid produced per litre and per hour.

EXAMPLE 7 - COMPARATIVE

Example 6 is repeated in the same apparatus and under the same operating conditions, but eliminating only the iron in the initial load and in the solution injected.

The oxygen consumption during the injection period is 0.44 l/min.

The following results are obtained:

- Degree of conversion (DC) of the
5 cyclohexane: 18.2 %
- ST of cyclohexanol relative to the
cyclohexane converted: 5.1 %
- ST of cyclohexanone relative to the
cyclohexane converted: 4.8 %
- 10 - ST of adipic acid relative to the
cyclohexane converted: 69.5 %
- ST of adipic acid + cyclohexanone +
cyclohexanol relative to the cyclohexane
converted: 79.4 %
- 15 - Molar ratio of adipic acid/total diacids
formed: 85.0 %

The production efficiency of the catalyst is 47.5 g of adipic acid produced per litre and per hour.

EXAMPLE 8 - COMPARATIVE

- 20 Example 7 is repeated in the same apparatus and under the same operating conditions, but eliminating the iron and chromium in the initial load and in the solution injected.

The oxygen consumption during the injection
25 period is 0.55 l/min.

The following results are obtained:

- Degree of conversion (DC) of the cyclohexane: 18.5 %
- ST of cyclohexanol relative to the cyclohexane converted: 10.8 %
- 5 - ST of cyclohexanone relative to the cyclohexane converted: 5.8 %
- ST of adipic acid relative to the cyclohexane converted: 61.6 %
- ST of adipic acid + cyclohexanone +
10 cyclohexanol relative to the cyclohexane converted: 78.2 %
- Molar ratio of adipic acid/total diacids formed: 84.0 %

The production efficiency of the catalyst is
15 56.5 g of adipic acid produced per litre and per hour.

Example 9 - Comparative

The ingredients below are loaded into a
125 ml titanium autoclave equipped with heating means
via a heating collar, a turbomixer and gas introduction
20 and pressure regulation means:

- 21.25 g (253 mmol) of cyclohexane
- 27.35 g of acetic acid
- 0.26 g (2.65 mmol) of cyclohexanone
- 0.0357 g (0.146 mmol of Mn) of manganese
25 acetate tetrahydrate
- 0.011 g of chromium acetate dihydrate
(0.04 mmol of Cr).

After closing the reactor, it is stirred at 1 000 rpm, an air pressure (100 bar at 20°C) is created and the reactor is heated. The temperature reaches 105°C in the bulk in 10 min and this temperature is 5 maintained for a further 150 min.

After cooling and depressurization, the reaction mixture consists of two liquid phases, which are homogenized by adding acetic acid.

The homogeneous mixture thus obtained is 10 assayed by gas chromatography.

The following results are obtained:

- Degree of conversion (DC) of the cyclohexane: 14.9 %
- ST of cyclohexanol relative to the cyclohexane converted: 19.4 %
- ST of cyclohexanone relative to the cyclohexane converted: 0.0 %
- ST of adipic acid relative to the cyclohexane converted: 50 %
- ST of adipic acid + cyclohexanone + cyclohexanol relative to the cyclohexane converted: 69.4 %
- Molar ratio of adipic acid/total diacids formed: 77.6 %

25 Example 10

Example 9 is repeated, but using as catalytic system the system having the following composition:

- 0.3107 g (1.247 mmol of Co) of cobalt acetate tetrahydrate
- 0.0119 g (0.012 mmol of Cr) of chromium acetate dihydrate
- 5 - 0.0861 g (0.244 mmol of Fe) of iron acetylacetonate
- 0.0525 g (0.149 mmol of Mn) of manganese(III) acetylacetonate.

The mixture is maintained at 105°C for
10 45 minutes.

The following results are obtained:

- Degree of conversion (DC) of the cyclohexane: 12.1 %
- ST of cyclohexanol relative to the cyclohexane converted: 9.5 %
- 15 - ST of cyclohexanone relative to the cyclohexane converted: 8.1 %
- ST of adipic acid relative to the cyclohexane converted: 67 %
- 20 - ST of adipic acid + cyclohexanone + cyclohexanol relative to the cyclohexane converted: 85.6 %
- Molar ratio of adipic acid/total diacids formed: 85.5 %

Example 11

Example 10 is repeated, but using as catalytic system the system having the following composition:

- 5 - 0.3135 g (1.258 mmol of Co) of cobalt acetate tetrahydrate
- 0.0114 g (0.0113 mmol of Cr) of chromium acetate dihydrate
- 0.0828 g (0.234 mmol of Fe) of iron
- 10 acetylacetonate
- 0.0522 g (0.148 mmol of Mn) of manganese(III) acetylacetonate
- 0.0059 g (0.0121 mmol of Zr) of zirconium acetylacetonate.

15 The following results are obtained:

- Degree of conversion (DC) of the cyclohexane: 11.7 %
- ST of cyclohexanol relative to the cyclohexane converted: 8.8 %
- 20 - ST of cyclohexanone relative to the cyclohexane converted: 9.4 %
- ST of adipic acid relative to the cyclohexane converted: 67.4 %
- ST of adipic acid + cyclohexanone +
- 25 cyclohexanol relative to the cyclohexane converted: 85.6 %

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- Molar ratio of adipic acid/total diacids
formed:

85.7 %

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CLAIMS

1. Process for oxidizing hydrocarbons, alcohols and/or ketones to carboxylic acid using oxygen or a gas containing it, in a liquid phase in a solvent
5 chosen from polar protic solvents and polar aprotic solvents and in the presence of a catalyst dissolved in the reaction medium, characterized in that the catalyst comprises a soluble manganese and/or cobalt compound, a soluble chromium compound and a soluble iron compound.
- 10 2. Process according to claim 1, characterized in that the hydrocarbon used as starting substrate is chosen from cycloalkanes which have a ring containing from 5 to 12 carbon atoms, and is preferably cyclohexane.
- 15 3. Process according to claim 1, characterized in that the alcohol and/or the ketone used as starting substrate are chosen from cycloalkanols and cycloalkanones which have a ring containing from 5 to 12 carbon atoms, and are
20 preferably cyclohexanol and/or cyclohexanone.
4. Process according to one of claims 1 to 3, characterized in that the catalyst comprises at least one manganese compound which is soluble in the reaction medium, chosen from manganese chloride,
25 manganese bromide, manganese nitrate and manganese carboxylates, for instance manganese acetate

tetrahydrate, manganese propionate, manganese adipate, manganese glutarate and manganese succinate.

5. Process according to one of claims 1 to 4, characterized in that the catalyst comprises at least one cobalt compound which is soluble in the reaction medium, chosen from cobalt chloride, cobalt bromide, cobalt nitrate and cobalt carboxylates, for instance cobalt acetate, cobalt propionate, cobalt adipate, cobalt glutarate and cobalt succinate.

10 6. Process according to one of claims 1 to 5, characterized in that the catalyst comprises at least one chromium compound which is soluble in the reaction medium, chosen from chromium chloride, chromium bromide, chromium nitrate and chromium
15 carboxylates, for instance chromium acetate, chromium propionate, chromium adipate, chromium glutarate, chromium succinate and mineral or organic chromic acid salts.

7. Process according to one of claims 1 to
20 6, characterized in that the catalyst comprises at least one iron compound which is soluble in the reaction medium, chosen from iron chloride, iron bromide, iron nitrate and iron carboxylates, for instance iron acetate, iron propionate, iron adipate,
25 iron glutarate and iron succinate.

8. Process according to one of the preceding claims, characterized in that the catalyst comprises a soluble zirconium or hafnium compound.

9. Process according to claim 8,
5 characterized in that the zirconium compound which is soluble in the reaction medium is chosen from zirconium chloride, zirconium bromide, zirconium nitrate and zirconium carboxylates, for instance zirconium acetate, zirconium propionate, zirconium adipate, zirconium
10 glutarate or zirconium succinate.

10. Process according to claim 8,
characterized in that the hafnium compound which is soluble in the reaction medium is chosen from hafnium chloride, hafnium bromide, hafnium nitrate and hafnium
15 carboxylates, for instance hafnium acetate, hafnium propionate, hafnium adipate, hafnium glutarate or hafnium succinate.

11. Process according to one of claims 1 to 10, characterized in that the molar ratios between the
20 chromium, the manganese or the cobalt, the chromium and the iron is between $1/0.00001/0.0001$ and $1/100/100$.

12. Process according to claim 11,
characterized in that the molar ratios between the chromium, the manganese or the cobalt, the chromium and
25 the iron is between $1/0.001/0.001$ and $1/10/10$.

13. Process according to one of claims 6 to 12, characterized in that the amount of catalyst, expressed as a weight percentage of metal elements relative to the reaction mixture, is between 0.0001% and 5% and preferably between 0.001% and 2%.

14. Process according to one of claims 1 to 13, characterized in that the liquid reaction medium contains a solvent chosen from aliphatic carboxylic acids containing from 2 to 9 carbon atoms, perfluoroalkylcarboxylic acids, alcohols, halogenated hydrocarbons, ketones, lower alkyl esters of carboxylic acids, preferably of aliphatic carboxylic acids containing from 2 to 9 carbon atoms or of perfluoroalkylcarboxylic acids, tetramethylene sulphone (or sulfolane) and acetonitrile.

15. Process according to one of claims 1 to 14, characterized in that the solvent used is acetic acid.

16. Process according to one of claims 1 to 15, characterized in that the solvent represents from 1% to 99% by weight of the reaction medium and preferably from 10% to 90.

17. Process according to one of claims 1 to 16, characterized in that the temperature at which the oxidation reaction is carried out is between 50°C and 200°C and preferably between 80°C and 140°C.

18. Process according to one of claims 1 to 17, characterized in that the pressure at which the oxidation reaction is carried out is between 0.1 MPa (1 bar) and 20 MPa (200 bar).