

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

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

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

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

Thus, US-A-2,223,493 describes the oxidation
20 of cyclic hydrocarbons into the 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 an oxidation catalyst
such as a cobalt compound.

25 US-A-3,987,100 describes a process for
preparing cyclohexanone and cyclohexanol by reaction of
cyclohexane with oxygen, in at least three successive

steps, at a temperature of 130°C to 180°C and under a pressure of about 4 to 25 bar and in the presence of very small amounts of a catalytic system comprising cobalt and chromium. This process is carried out
5 without solvent and does not allow adipic acid to be prepared directly.

GB-A-1,086,951 describes the combined oxidation of mixtures of cyclohexanol and an aldehyde, in the liquid phase, with oxygen, in the absence or
10 presence of a catalyst comprising at least one transition metal compound. This process leads to cyclohexanone, ϵ -caprolactone and dicarboxylic acids starting from cyclohexanol, and to the monocarboxylic acid corresponding to the aldehyde used.

15 US-A-4,902,827 describes an improvement to the air-oxidation of cyclohexane into adipic acid, in a liquid phase containing acetic acid, at a temperature of 80°C to 160°C and in the presence of an oxidation catalyst comprising a soluble cobalt compound and a
20 soluble zirconium and/or hafnium compound.

More recently, EP-A-0,694,333 has recommended using a catalyst comprising a cobalt salt and a ferric salt in the context of the oxidation of hydrocarbons with oxygen.

25 Nevertheless, it turns out that the selectivities obtained with the catalytic systems used in the prior processes described above must still be improved.

It is this improvement which the present invention proposes to achieve. The present invention provides a process for the liquid phase oxidation of a hydrocarbon, an alcohol and/or a ketone, generally into
5 carboxylic acid, using oxygen or a gas containing it, in a polar protic solvent or a polar aprotic solvent and in the presence of a catalyst dissolved in the reaction medium, wherein the catalyst comprises at least one cobalt compound and at least one chromium
10 compound, the cobalt compound and the chromium compound being soluble in the reaction medium.

The hydrocarbons used as starting substrates in the process of the invention are preferably alkanes, cycloalkanes, alkylaromatic hydrocarbons, alkenes and
15 cycloalkenes, having from 3 to 20 carbon atoms.

Among these hydrocarbons, cycloalkanes, in particular those which have a ring having from 5 to 12 carbon atoms, are certainly the most preferred, since their oxidation leads to dicarboxylic acids and in
20 smaller proportions to intermediate cycloalkanols and cycloalkanones.

The present invention includes processes wherein a hydrocarbon is oxidised to a corresponding alcohol or ketone.

25 The most advantageous hydrocarbon is cyclohexane, which can be oxidised to adipic acid, one of the base compounds of polyamide 6-6.

The present process can also be used for the

oxidation of the intermediate alcohols or ketones, in particular cycloalkanols and cyclohexanones having from 5 to 12 carbon atoms, in order to prepare the corresponding dicarboxylic acids. In the text
5 hereinbelow, the process will be described more particularly for the oxidation of hydrocarbons, essentially cycloalkanes, and more especially for the oxidation of cyclohexane.

The catalyst comprising at least one cobalt
10 compound and a chromium compound makes it possible to prepare directly adipic acid with good selectivity, when the oxidation of cyclohexane is carried out; this capacity is obviously very advantageous.

The catalyst comprises at least one cobalt
15 compound which is soluble in the reaction medium, chosen, for example, from cobalt chloride, cobalt bromide, cobalt nitrate, cobalt carboxylates such as cobalt acetate tetrahydrate, cobalt propionate, cobalt adipate, cobalt glutarate, cobalt succinate and cobalt
20 chelates such as cobalt acetylacetonate.

The catalyst also comprises 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
25 nitrate, chromium carboxylates such as chromium acetate, chromium propionate, chromium adipate, chromium glutarate, chromium succinate and chromium chelates such as chromium acetylacetonate.

The molar ratio between the chromium and the cobalt in the catalyst can vary within a wide range. Typically, the Cr/Co molar ratio is from 0.001 to 100 and preferably from 0.01 to 10.

5 The catalyst can be prepared in situ by loading the cobalt and chromium compounds into the reaction medium. It can also be prepared at the time of use by mixing the said compounds in the proportions required to obtain the desired Cr/Co molar ratio. This
10 mixing is more conveniently carried out in a solvent, preferably the solvent which will be used for the oxidation reaction.

 The catalyst used in the process of the invention can also comprise at least one zirconium
15 and/or hafnium compound which is soluble in the reaction medium. As examples, the zirconium and hafnium compounds can be chosen from zirconium tetrachloride, zirconium bromide, zirconium nitrate, zirconium carboxylates such as zirconium acetate, zirconium
20 propionate, zirconium adipate, zirconium glutarate, zirconium succinate, zirconium chelates such as zirconium acetylacetonate, hafnium chloride, hafnium bromide, hafnium nitrate, hafnium carboxylates such as hafnium acetate, hafnium propionate, hafnium adipate,
25 hafnium glutarate, hafnium succinate and hafnium chelates such as hafnium acetylacetonate.

 The molar ratio between the zirconium and/or hafnium and the cobalt in the catalyst is typically

from 0 to 10 and preferably from 0.001 to 5.

The amount of catalyst, expressed as a weight percentage of elemental cobalt and of elemental chromium relative to the reaction mixture, is generally
5 from 0.001% to 5% and preferably from 0.01% to 2%. It is a case, however, of having a sufficient activity while at the same time not using excessive amounts of a catalyst which then needs to be separated from the final reaction mixture and recycled.

10 It is advantageous also to use an initiator compound for the oxidation reaction. Suitable initiators include hydroperoxides such as cyclohexyl hydroperoxide or tert-butyl hydroperoxide. They are also ketones or aldehydes such as cyclohexanone, which
15 is one of the compounds formed during the oxidation of cyclohexane, or acetaldehyde. Generally, the initiator represents from 0.01% to 20% by weight relative to the weight of the reaction mixture used. The initiator is especially useful during the beginning of the oxidation
20 and when the oxidation of cyclohexane is carried out at a temperature below 120°C. It can be introduced from the start of the reaction.

The liquid reaction medium contains a solvent in which the carboxylic acid which it is intended to
25 prepare by carrying out the process of the invention is at least sparingly soluble. This solvent can be very varied in nature, provided that it is not substantially oxidizable under the reaction conditions. It can be

chosen from polar protic solvents and polar aprotic solvents. As polar protic solvents, mention may be made, for example, of carboxylic acids having only primary or secondary hydrogen atoms, in particular
5 aliphatic acids having from 2 to 9 carbon atoms, perfluoroalkylcarboxylic acids such as trifluoroacetic acid, alcohols such as tert-butanol, halogenated hydrocarbons such as dichloromethane, and ketones such as acetone. As polar aprotic solvents, mention may be
10 made, for example, of lower alkyl esters in which the alkyl moiety typically has from 1 to 4 carbon atoms of carboxylic acids, in particular aliphatic carboxylic acids having from 2 to 9 carbon atoms or perfluoroalkylcarboxylic acids, tetramethylenesulphone
15 (or sulfolane), or acetonitrile.

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

The solvent, as defined above, generally
25 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 can 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
5 depending on the substrate used. It is generally from 50°C to 200°C and preferably from 80°C to 140°C.

The pressure is not a critical parameter of the process. It can be less than, equal to or greater than atmospheric pressure. Generally, it will be from
10 0.1 MPa (1 bar) to 20 MPa (200 bar).

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

The Examples which follow illustrate the
15 invention.

EXAMPLE 1

The following reactants:

- 21.25 g (253 mmol) of cyclohexane
- 27.35 g of acetic acid
- 20 - 0.26 g (2.65 mmol) of cyclohexanone
- 0.32 g (1.29 mmol of Co) of cobalt acetate tetrahydrate
- 0.0331 g (0.1445 mmol of Cr) of chromium acetate

25 are loaded into a 125 ml titanium autoclave fitted with means for heating via a heating collar, a turbine mixer and means for introducing gas and regulating the

pressure.

After closing the reactor, it is stirred at 1000 revolutions per minute, an air pressure (100 bar at 20°C) is created and the reactor is heated. The
 5 temperature reaches 105°C in the bulk in 10 min and this temperature is maintained for a further 50 min.

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

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

The following results are obtained:

	- degree of conversion (DC)	
	of the cyclohexane:	12.2%
15	- selectivity (CS) towards cyclohexanol relative to the cyclohexane converted:	6.2%
	- selectivity (CS) towards cyclohexanone relative to the cyclohexane converted:	11.9%
20	- CS towards adipic acid relative to the cyclohexane converted:	67.3%
	- CS towards adipic acid + cyclohexanone + cyclohexanol relative to the cyclohexane converted:	85.4%
25	- molar ratio of adipic acid/total of the diacids formed (adipic acid, glutaric acid and succinic acid):	85.3%

- CS towards other compounds (butyrolactone, valerolactone, hydroxyadipic acid, hydroxycaproic acid): 3.0%

COMPARATIVE TEST 1

- 5 Example 1 is repeated in the same apparatus and under the same operating conditions, but without loading any chromium compound and using an amount of cobalt acetate tetrahydrate increased by an amount equal to the molar amount of chromium acetate in
- 10 Example 1. The following results are obtained:
- degree of conversion (DC) of the cyclohexane: 15.0%
 - CS towards cyclohexanol relative to the cyclohexane converted: 14.7%
 - 15 - CS towards cyclohexanone relative to the cyclohexane converted: 8.1%
 - CS towards adipic acid relative to the cyclohexane converted: 54.7%
 - CS towards adipic acid + cyclohexanone + cyclohexanol relative to the cyclohexane converted: 77.5%
 - 20 - molar ratio of adipic acid/total of the diacids formed: 82.6%
 - CS towards other compounds: 10.9%

25 COMPARATIVE TEST 2

Comparative test 1 is repeated in the same

apparatus and under the same operating conditions, but using an even larger amount of cobalt acetate tetrahydrate (1.45 g).

The following results are obtained:

5	- degree of conversion (DC)	
	of the cyclohexane:	13.2%
	- CS towards cyclohexanol relative	
	to the cyclohexane converted:	9.5%
	- CS towards cyclohexanone relative	
10	to the cyclohexane converted:	8.5%
	- CS towards adipic acid relative to the	
	cyclohexane converted:	56.7%
	- CS towards adipic acid + cyclohexanone	
	+ cyclohexanol relative to the cyclo-	
15	hexane converted:	74.7%
	- molar ratio of adipic acid/total of	
	the diacids formed:	81.2%
	- CS towards other compounds:	12.2%

COMPARATIVE TEST 3

20 Example 1 is repeated in the same apparatus and under the same operating conditions, but replacing the chromium acetate by the same molar amount of iron acetate.

The following results are obtained:

25	- degree of conversion (DC)	
	of the cyclohexane:	15.0%
	- CS towards cyclohexanol relative	

	to the cyclohexane converted:	9.3%
	- CS towards cyclohexanone relative	
	to the cyclohexane converted:	7.3%
	- CS towards adipic acid relative to the	
5	cyclohexane converted:	58.9%
	- CS towards adipic acid + cyclohexanone	
	+ cyclohexanol relative to the cyclo-	
	hexane converted:	75.5%
	- molar ratio of adipic acid/total of	
10	the diacids formed:	81.0%
	- CS towards other compounds:	10.7%

COMPARATIVE TEST 4

Example 1 is repeated in the same apparatus and under the same operating conditions, but replacing
 15 the chromium acetate by the same molar amount of manganese acetate.

The following results are obtained:

	- degree of conversion (DC)	
	of the cyclohexane:	13.9%
20	- CS towards cyclohexanol relative	
	to the cyclohexane converted:	17.1%
	- CS towards cyclohexanone relative	
	to the cyclohexane converted;	8.1%
	- CS towards adipic acid relative to the	
25	cyclohexane converted:	54.2%
	- CS towards adipic acid + cyclohexanone	
	+ cyclohexanol relative to the cyclo-	

hexane converted:	79.4%
- molar ratio of adipic acid/total of the diacids formed:	83.4%
- CS towards other compounds:	9.8%

5 COMPARATIVE TEST 5

The following reactants:

- 47.4 g of acetic acid
- 0.25 g (2.54 mmol) of cyclohexanone
- 1.72 g (6.88 mmol of Co) of cobalt acetate
10 tetrahydrate
- 0.194 g (1.11 mmol of Fe) of iron acetate

are loaded into the apparatus described in Example 1.

After closing the reactor, the mixture is stirred at 1000 revolutions per minute, an air pressure
15 (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 maintained for a further 50 min.

After cooling and depressurization, 10.1 g of cyclohexane are then added. After closing the reactor,
20 a pressure of 100 bar of air is established and the reactor is heated to 105°C with stirring at 1000 revolutions/minute.

The mixture is left to react for 1 hour at 105°C while keeping the pressure constant using a
25 reserve of pure oxygen.

After cooling and depressurizing the reactor, the reaction mixture consists of two liquid phases

which are homogenized by adding acetic acid.

The homogeneous mixture thus obtained is assayed by gas chromatography.

The following results are obtained:

5	- degree of conversion (DC)	
	of the cyclohexane:	40.9%
	- CS towards cyclohexanol relative	
	to the cyclohexane converted:	9.6%
	- CS towards cyclohexanone relative	
10	to the cyclohexane converted:	0%
	- CS towards adipic acid relative to the	
	cyclohexane converted:	66.8%
	- CS towards adipic acid + cyclohexanone	
	+ cyclohexanol relative to the cyclo-	
15	hexane converted:	76.4%
	- molar ratio of adipic acid/total of	
	the diacids formed:	81.1%
	- CS towards other compounds:	8.2%

EXAMPLE 2

20 Example 1 is repeated in the same apparatus, under the same temperature and pressure conditions and with the same reactants, but with a reaction time of 115 min.

The following results are obtained:

25	- degree of conversion (DC)	
	of the cyclohexane:	15.0%
	- CS towards cyclohexanol relative	

	to the cyclohexane converted:	4.3%
	- CS towards cyclohexanone relative	
	to the cyclohexane converted:	0%
	- CS towards adipic acid relative to the	
5	cyclohexane converted:	75.2%
	- CS towards adipic acid + cyclohexanone	
	+ cyclohexanol relative to the cyclo-	
	hexane converted:	79.5%
	- molar ratio of adipic acid/total of	
10	the diacids formed:	83%
	- CS towards other compounds:	5.0%

EXAMPLE 3

Example 2 is repeated in the same apparatus,
under the same operating conditions and with the same
15 reactants, but adding 0.0049 g (0.01 mmol of Zr) of
zirconium acetylacetonate and with a reaction time of
35 min.

The following results are obtained:

	- degree of conversion (DC)	
20	of the cyclohexane:	14.1%
	- CS towards cyclohexanol relative	
	to the cyclohexane converted:	4.8%
	- CS towards cyclohexanone relative	
	to the cyclohexane converted:	10.0%
25	- CS towards adipic acid relative to the	
	cyclohexane converted:	67.1%
	- CS towards adipic acid + cyclohexanone	

	+ cyclohexanol relative to the cyclo-	
	hexane converted:	81.9%
	- molar ratio of adipic acid/total of	
	the diacids formed:	84.5%
5	- CS towards other compounds:	5.8%

EXAMPLE 4

Example 1 is repeated in the same apparatus and under the same operating conditions, but using
 10 0.0672 g (0.29 mmol of Cr) of chromium acetate and with a reaction time of 115 min.

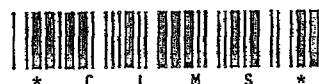
The following results are obtained:

	- degree of conversion (DC)	
	of the cyclohexane:	14.6%
15	- CS towards cyclohexanol relative	
	to the cyclohexane converted:	4.5%
	- CS towards cyclohexanone relative	
	to the cyclohexane converted:	3.5%
	- CS towards adipic acid relative to the	
20	cyclohexane converted:	72.9%
	- CS towards adipic acid + cyclohexanone	
	+ cyclohexanol relative to the cyclo-	
	hexane converted:	80.8%
	- molar ratio of adipic acid/total of	
25	the diacids formed:	84.7%
	- CS towards other compounds:	6.0%

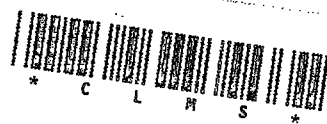
EXAMPLE 5

Example 1 is repeated in the same apparatus and under the same operating conditions, but using 0.0033 g (0.0145 mmol of Cr) of chromium acetate and with a reaction time of 60 min.

- 5 The following results are obtained:
- degree of conversion (DC)
 - of the cyclohexane: 14.0%
 - CS towards cyclohexanol relative
 - to the cyclohexane converted: 7.6%
 - 10 - CS towards cyclohexanone relative
 - to the cyclohexane converted: 14.7%
 - CS towards adipic acid relative to the
 - cyclohexane converted: 59.4%
 - CS towards adipic acid + cyclohexanone
 - 15 + cyclohexanol relative to the cyclo-
 - hexane converted: 81.7%
 - molar ratio of adipic acid/total of
 - the diacids formed: 83.7%
 - CS towards other compounds: 6.5%

CLAIMS

1. A process for the liquid phase oxidation of a hydrocarbon, an alcohol and/or a ketone using oxygen or a gas containing it, in a polar protic solvent or a polar aprotic solvent and in the presence of a catalyst dissolved in the reaction medium, wherein the catalyst comprises at least one cobalt compound and at least one chromium compound, the cobalt compound and the chromium compound being soluble in the reaction medium.
2. A process according to claim 1, wherein the hydrocarbon is a cycloalkane having from 5 to 12 carbon atoms, and is preferably cyclohexane.
3. A process according to claim 1 or 2, wherein the hydrocarbon, alcohol and/or ketone is oxidised to a corresponding carboxylic acid.
4. A process according to any one of the preceding claims, wherein the alcohol and/or the ketone is a cycloalkanol or cycloalkanone having from 5 to 12 carbon atoms, preferably cyclohexanol and/or cyclohexanone.
5. A process according to any one of the preceding claims, wherein the said cobalt compound is chosen from cobalt chloride, cobalt bromide, cobalt nitrate, cobalt carboxylates and cobalt chelates.
6. A process according to any one of the preceding claims, wherein the said chromium compound is chosen from chromium chloride, chromium bromide, chromium nitrate, chromium carboxylates and chromium chelates.
7. A process according to any one of the preceding claims, wherein the molar ratio chromium: cobalt in the catalyst is from 0.001:1 to 100:1, preferably from 0.01:1 to 10:1.
8. A process according to any one of the preceding claims, wherein the catalyst further



comprises at least one zirconium and/or hafnium compound which is soluble in the reaction medium, chosen from zirconium tetrachloride, zirconium bromide, zirconium nitrate, zirconium carboxylates, zirconium
5 chelates, hafnium chloride, hafnium bromide, hafnium nitrate, hafnium carboxylates and hafnium chelates.

9. A process according to claim 8, wherein the molar ratio zirconium and/or hafnium:cobalt in the catalyst is up to 10:1, preferably from 0.001:1 to 5:1.

10 10. A process according to any one of the preceding claims, wherein the amount of catalyst, expressed as a weight percentage of elemental cobalt and of elemental chromium relative to the reaction mixture, is from 0.001% to 5%, preferably from 0.01% to
15 2%.

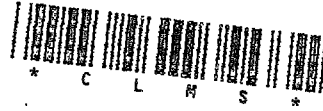
11. A process according to any one of the preceding claims, wherein the solvent is chosen from aliphatic carboxylic acids having from 2 to 9 carbon atoms, perfluoroalkylcarboxylic acids, alcohols,
20 halogenated hydrocarbons, ketones, lower alkyl esters of carboxylic acids, preferably aliphatic carboxylic acids having from 2 to 9 carbon atoms or perfluoroalkylcarboxylic acids, tetramethylene sulphone (or sulfolane) and acetonitrile.

25 12. A process according to claim 11, wherein the solvent is acetic acid.

13. A process according to any one of the preceding claims, wherein the solvent represents from 1% to 99% by weight of the reaction medium, preferably
30 from 10% to 90% and even more preferably from 20% to 80%.

14. A process according to any one of the preceding claims, wherein the temperature at which the oxidation reaction is carried out is from 50°C to 200°C
35 and preferably from 80°C to 140°C.

15. A process according to any one of the preceding claims, wherein the pressure at which the



oxidation reaction is carried out is from 0.1 MPa (1 bar) to 20 MPa (200 bar).

16. A process according to any one of the preceding claims, substantially as hereinbefore
5 described in any one of Examples 1 to 5.

17. A process according to any one of the preceding claims, wherein cyclohexane is oxidised to adipic acid.

18. A process for preparing polyamide 6,6,
10 which process comprises:

(a) preparing adipic acid by a process according to claim 17; and

(b) using the thus obtained adipic acid to prepare polyamide 6,6.

19. A compound prepared by a process
15 according to any one of the preceding claims.