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(54) **Title**: CATALYSED CYCLOHEXANE OXIDATION

(57) **Abstract**: The invention is directed to a method for preparing a mixture comprising cyclohexanol and cyclohexanone. In accordance with the invention a mixture comprising cyclohexanol and cyclohexanone is prepared in a molar cyclohexanone/cyclohexanol ratio of at least 1.2 at a cyclohexane conversion of below 5 mol%. The method comprises oxidising cyclohexane in a liquid phase, said oxidising being catalysed by a cobalt compound and a chromium compound, wherein the atomic cobalt to chromium ratio is in the range of 0.05-0.8, wherein the sum of the concentrations of cobalt and chromium is 0.05-0.9 ppm by weight based on the total weight of the reaction mixture, and wherein the cobalt compound and chromium compound are dissolved in the liquid phase.

CATALYSED CYCLOHEXANE OXIDATION

The invention is directed to a method for preparing a mixture comprising cyclohexanol and cyclohexanone.

Cyclohexanol and cyclohexanone can be commercially produced from cyclohexane. The first step in such a process is oxidation of the cyclohexane by an oxygen-containing gas to produce cyclohexanol, cyclohexanone and cyclohexylhydroperoxide. The mixture of cyclohexanol (A) and cyclohexanone (K) is commonly referred to as "KA". Conventionally, in this first step cylcohexane is oxidised in the liquid phase with air. This oxidation is normally conducted on industrial scale, either uncatalysed or with a soluble cobalt catalyst, in one or more reactors at temperatures in the range of 130-200 °C. The vaporised cyclohexane and other products in the gaseous effluent are condensed and recovered, and the off-gases leave the system. The KA product is recovered from the liquid effluent from the reactor or reactors, and the unreacted cyclohexane is recycled (Kirk-Othmer, *Encyclopedia of Chemical Technology*, John-Wiley & Sons, New York, 1979, 3rd Edition, Vol. 7, pp. 410-416 and Ullmanns, *Encyklopädie der technischen Chemie*, Verlag Chemie, Weinheim, 1975, 4th Edition, Vol. 9, pp. 689-698).

A process of oxidising cyclohexane to produce a product essentially consisting of cyclohexanone and cyclohexanol in the presence of a binary catalyst system of cobalt and chromium is known from US-A-3 987 100. The only cobalt to chromium ratios disclosed for the step wherein cyclohexane is oxidised are in the preferred embodiment (Examples, Table 2), mentioning a cobalt concentration of 0.1 ppm and a chromium concentration of 0.04 ppm, which corresponds to an atomic ratio of cobalt to chromium of 2.2. Hence, there is always more cobalt present than chromium. In addition, it is not specified whether the ratio of cobalt to chromium has an effect on the oxidation process.

US-A-3 598 869 describes a process wherein cyclohexane is oxidised to obtain a mixture of (a) cyclohexanol and cyclohexanone (KA) and (b) a mixture of carboxylic acid derivatives of cyclohexane (COP acids) in a particularly suitable ratio (*i.e.* of about 1:1) of COP acids to KA for further conversion to nylon salts in the presence of at least one catalyst of the group of cobalt and chromium. Catalyst concentrations can be between 1 ppm and 200 ppm, calculated as the metal, or higher. In a preferred embodiment chromium is used and no cobalt. Moreover, it is noted that

this document discloses high cyclohexane conversions such as in between about 14 mol% and 30 mol%.

EP-A-0 063 931 relates to a process for the catalytic oxidation of a liquid cycloparaffin to partial oxidation products thereof, which comprises introducing amolecular oxygen-containing gas into a cycloparaffin of from 5 to 12 carbon atoms in the presence of an oxidation catalyst comprising a combination of a cobalt compound and a chromium compound, said oxidation catalyst being soluble in the cycloparaffin, said cobalt compound having ligands selected from the group consisting of dialkyl phosphate, dicycloalkylphosphate and alkylcycloalkylphosphate, and mixtures thereof, the ratio of cobalt compound to chromium compound being greater than 1:1 on an atomic basis. This means that there is more cobalt than chromium.

SU-A-929 213 describes a catalyst for the oxidation of pure cyclohexane. Although two experiments are shown with different cobalt to chromium ratios (respectively of 38 vs. 62 %; and of 23 vs. 77 % of the naphthenates), both experiments show substantially the same selectivity. In addition, the concentration of the sum of cobalt and chromium in the reaction medium is 1 ppm by weight in each of these experiments, and the cyclohexane conversion is higher than 5 mol%. Furthermore, the highest K/A ratio is 1.05.

It is an object of the invention to provide a novel process for the preparation of a mixture comprising cyclohexanol and cyclohexanone, with improved selectivity towards desired products, namely cyclohexylhydroperoxide, cyclohexanol and cyclohexanone, while at the same time obtaining a high molar cyclohexanone/cyclohexanol ratio (K/A ratio) in comparison with processes described in the prior art. A precise definition of the term “selectivity” as used herein is given hereinafter.

One or more objects which may be accomplished in accordance with the invention will become apparent from the description and/or claims below.

It has now been found possible to meet at least one of said objects by oxidising cyclohexane in the presence of a specific form of catalytic cobalt and a specific form of catalytic chromium, and using said catalysts in a specific ratio and under specific conditions.

Accordingly, in a first aspect the invention is directed to a method for preparing, at high selectivity towards desired products, a mixture comprising cyclohexanol and cyclohexanone in a molar cyclohexanone/cyclohexanol ratio of at least 1.2 and with a cyclohexane conversion below 5 mol%, comprising oxidising cyclohexane in a liquid phase, said oxidising being catalysed by a cobalt compound

and a chromium compound, the atomic cobalt to chromium ratio being in the range of 0.05 to 0.8, wherein the sum of the concentrations of cobalt and chromium is 0.05-0.9 ppm by weight based on the total weight of the reaction mixture, and wherein the cobalt compound and chromium compound are dissolved in the liquid phase.

The inventors found that the process of the invention, wherein a specific cobalt chromium catalyst is utilised at a cyclohexane conversion below 5 mol%, advantageously allows achieving, at a specific conversion level (*e.g.* of 3 or 4 mol%), both a high value of K/A and a higher selectivity than is achieved with prior art processes. Selectivity in this regard is defined as the sum of desired products (cyclohexanol, cyclohexanone, and cyclohexylhydroperoxide) divided by the total amount of cyclohexane that has been converted on a molar basis. Moreover, the process of the invention at the same time yields an advantageously high K/A ratio (such as a molar K/A ratio of 1.2 or more, or even a molar K/A ratio of 1.4 or more). A high K/A ratio is desirable, because it minimises subsequent conversion of remaining cyclohexanol to the final product cyclohexanone. The K/A ratio can for instance be as high as 1.6.

The catalyst used in the process of the invention is a combination of a cobalt compound and a chromium compound. The term “compound” as used in this context includes complexes, salts, and the like. In the cobalt compound, the cobalt can be present either as Co^{II} or as Co^{III}. In terms of solubility, compounds wherein the cobalt is present as Co^{II} are preferred. In the chromium compound, the chromium can be present as Cr^{III} or even higher oxidation states. In practice, the chromium will usually be present as Cr^{III} in the chromium compound.

Suitably, the cobalt compound and/or chromium compound can comprise one or more ligands selected from porphyrins, phthalocyanines, 1,3-bis(arylimino) isoindolines, Schiff bases, hydroxides, carboxylates (such as acetates, propanoates, butyrates, octanoates, benzoates, naphthenates, and stearates), picolinates, acetylacetonates and other beta-diketones, 1,3-bis(arylimino) isoindolinates, salen, saleph, porphyrinates, porphycenates, porphenates, phthalocyanates, bipyridines, terpyridines, phenanthrolines, dithiocarbamates, xanthates, salicylaldimines, cyclam, dioxocyclam, pyrazoylborates, and tetraazamacrocyclic compounds. In particular, the cobalt compound and/or chromium compound can comprise one or more ligands selected from the group consisting of acetylacetonates, octanoates, naphthenates, bipyridines, porphyrinates, and phthalocyanates. In case the cobalt compound and/or chromium compound comprise one or more ligands, the one or more ligands can be present in excess.

In the process of the invention, the atomic ratio of cobalt to chromium in the oxidation catalyst of cyclohexane is in the range of 0.05-0.8. In particular, the ratio of cobalt to chromium can be in the range of 0.1-0.5, more in particular in the range of 0.15-0.35. The atomic ratio of cobalt to chromium in the catalyst is of particular importance in obtaining a product having a high K/A ratio, along with a high selectivity. It was found that either the K/A ratio or the selectivity considerably decreases if the atomic cobalt to chromium ratio is higher than 0.8 and/or if the total metal concentration is higher than 0.9 ppm. On the other hand, if the amount of cobalt becomes too low, such the atomic ratio of cobalt to chromium in the catalyst becomes lower than 0.05, the K/A ratio remains high but the selectivity drops to too low values (e.g. to less than 86% at 3 mol% conversion; respectively less than 84% at 4 mol% conversion).

Furthermore, the cobalt compound and the chromium compound are dissolved in the liquid phase. This means that the cobalt/chromium catalyst is a homogeneous catalyst. In an advantageous embodiment, the cyclohexane oxidation process of the invention is a homogeneous catalysis process.

The selectivity and/or the K/A ratio were found to increase, generally at decreasing values for the sum of the concentrations of cobalt and chromium, at an atomic ratio of cobalt to chromium in the range of from 0.05 to 0.8, and at conversions in the range of from 3 mol% to just below 5 mol%. The optimum of the total concentration of cobalt and chromium is in the range of from 0.05 to 0.9 ppm.

Thus, according to the invention, the sum of the concentrations cobalt and chromium is 0.05-0.9 by weight based on the total weight of the reaction mixture, in particular 0.1-0.7 ppm by weight, more in particular 0.2-0.6 ppm by weight, especially at about 0.5 ppm.

The cobalt concentration during the oxidation reaction can suitably be 0.01-0.4 ppm by weight of the total reaction mixture, in particular 0.05-0.2 ppm by weight. The chromium concentration during the oxidation reaction can suitably be 0.04-0.8 ppm by weight of the total reaction mixture, in particular 0.1-0.5 ppm by weight. Such low amounts of cobalt and chromium are advantageous in view of environmental aspects, as well as in reducing fouling problems. Moreover, it was found that these relatively low amounts of catalyst still yield satisfactorily high conversion (such as 2-just below 5 mol%) with acceptable residence times.

The process of the invention has a cyclohexane conversion of below 5 mol%, in particular of 2.5-4.5 mol%, more in particular 3-4 mol%. The conversion can largely be influenced by the residence time of the reaction products in the oxidising reactor(s). A cyclohexane conversion of below 5 mol% is advantageous, because the

selectivity decreases quickly at or above a conversion of 5 mol%. At a conversion below 2.5 mol%, and in particular at a conversion below 2 mol%, the amount of cyclohexane to be evaporated becomes rather high.

The cyclohexane oxidation of the invention can suitably be conducted in a reactor system, comprising one or more oxidation reactors (such as 3-8), which system preferably has plug flow characteristics, such as multiple reactors in series, for instance multiple CSTRs (Continuous Stirred Tank Reactors) in series or multiple bubble columns in series. Normally, the reaction temperature will normally be at least 130 °C, in particular at least 140 °C. It is not preferred that the reaction temperature exceeds 180 °C, in particular 170 °C, because at higher temperatures there is so much decomposition of cyclohexylhydroperoxide that the selectivity goes down. Depending on the temperature and the pressure during the reaction, the residence time is usually in the range of 1-120 minutes, such as 5-90 minutes, in particular 10-60 minutes.

After appropriate purification (which typically involves a number of distillation steps) the cyclohexanone/cyclohexanol mixture can be used for the preparation of adipic acid. Furthermore, after appropriate isolation of cyclohexanone from the obtained mixture, the isolated cyclohexanone can be used for the preparation of cyclohexanone oxime, caprolactam and nylon.

The invention is further demonstrated by the following examples and comparative examples. In the experimental part the following abbreviations are used:

acac: acetylacetonate
EH: 2-ethylhexanoate
which is often also referred to as octanoate
CH_x: cyclohexane
NL/hr: normal litre per hour

Examples

Comparative Example A

A mixture of 96.26 g of a cyclohexane feed as used in a cyclohexane oxidation plant (hereinafter referred to as "CH_x feed"), 1.0326 g of biphenyl (internal standard), and 0.1673 g of a solution of $Cr(acac)_3$ in cyclohexane (249.9 ppm Cr) was placed in a Hastelloy fed-batch reactor. In this comparative example only chromium was used with a concentration of 0.43 ppm in the CH_x feed. The system was pressurised with N_2 up to 10-11 bar and heated up to 156 °C under a 30 NL/h nitrogen flow while stirring at a rate of 1300 rpm. At reaction temperature, the nitrogen flow was changed for a 30 NL/h flow of 14 % O_2 in N_2. Samples were taken at regular intervals

and analysed by gas chromatography. During reaction, CO and CO_2 were continuously monitored in the off-gas.

Comparative Example B

A mixture of 97.80 g of CH_x feed, 1.0090 g of biphenyl (internal standard), and 0.3364 g of a solution of $Cr(acac)_3$ in cyclohexane (249.9 ppm Cr) was placed in the same reactor as comparative example A. In the present comparative example only chromium was used with a concentration of 0.86 ppm in the CH_x feed. The reaction was carried out using the same conditions and in the same way as in Comparative Example A.

Comparative Example C

A mixture of 98.20 g of CH_x feed, 1.0254 g biphenyl (internal standard), 0.34901 g of a solution of $Cr(acac)_3$ in cyclohexane (249.9 ppm Cr) and 0.67525 g of a solution of $Co(EH)_2$ in cyclohexane (149 ppm Co) was placed in the same reactor as comparative example A. In the present comparative example the chromium and cobalt concentrations used were 0.88 ppm and 1.02 ppm in the CH_x feed, respectively, giving an atomic Co/Cr ratio of 1.02. The reaction was carried out using the same conditions and in the same way as in Comparative Example A.

Comparative Example D

A mixture of 96.97 g of CH_x feed, 1.0880 g of biphenyl (internal standard), 0.9147 g of a solution of $Cr(acac)_3$ in cyclohexane (60.52 ppm Cr) and 0.6716 g of a solution of $Co(EH)_2$ in cyclohexane (149 ppm Co) was placed in the same reactor as comparative example A. In the present comparative example the chromium and cobalt concentrations used were 0.57 ppm and 0.35 ppm in the CH_x feed, respectively, giving a molar ratio of 1.60. The reaction was carried out using the same conditions and in the same way as in Comparative Example A.

Comparative Example E

A mixture of 99.21 g of CH_x feed, 1.0002 g of biphenyl (internal standard), 0.0389 g of a solution of $Co(EH)_2$ in cyclohexane (637 ppm Co) was placed in the same reactor as comparative example A. In the present comparative example only cobalt was used with a concentration of 0.25 ppm in the CH_x feed. The reaction was carried out using the same conditions and in the same way as in Comparative Example A.

Comparative Example F.

A mixture of 98.85 g of CH_x feed, 1.0074 g of biphenyl (internal standard), 0.33 g of a solution of $Co(EH)_2$ in cyclohexane (149 ppm Co) was placed in the same reactor as comparative example A. In the present comparative example only cobalt was used with a concentration of 0.50 ppm in the CH_x feed. The reaction was carried out using the same conditions and in the same way as in Comparative Example A.

Comparative Example G

A mixture of 95.66 g of CH_x feed, 1.0186 g of biphenyl (internal standard), 1.1798 g of a solution of $Cr(acac)_3$ in cyclohexane (60.52 ppm Cr) and 0.1716 g of a solution of $Co(EH)_2$ in cyclohexane (149 ppm Co) was placed in the same reactor as comparative example A. In the present comparative example the chromium and cobalt concentrations used were 0.75 ppm and 0.27 ppm in the CH_x feed, respectively, giving a molar ratio of 0.32. The reaction was carried out using the same conditions and in the same way as in Comparative Example A.

Comparative Example H

A mixture of 101.90 g of CH_x feed, 1.0345 g of biphenyl (internal standard), 1.086 g of a solution of $Cr(acac)_3$ in cyclohexane (60.52 ppm Cr) and 0.2130 g of a solution of $Co(EH)_2$ in cyclohexane (149 ppm Co) was placed in the same reactor as comparative example A. In the present comparative example the chromium and cobalt concentrations used were 0.65 ppm and 0.31 ppm in the CH_x feed, respectively, giving a molar ratio of 0.42. The reaction was carried out using the same conditions and in the same way as in Comparative Example A.

Comparative Example I

A mixture of 99.85 g of CH_x feed, 1.2357 g of biphenyl (internal standard), 7.849 g of a solution of $Cr(acac)_3$ in cyclohexane (60.52 ppm Cr) and 0.725 g of a solution of $Co(EH)_2$ in cyclohexane (149 ppm Co) was placed in the same reactor as comparative example A. In the present comparative example the chromium and cobalt concentrations used were 4.4 ppm and 1.0 ppm in the CH_x feed, respectively, giving a molar ratio of 0.2. The reaction was carried out using the same conditions and in the same way as in Comparative Example A.

Example 1

A mixture of 95.52 g of CH_x feed, 1.0189 g of biphenyl (internal standard), 0.74260 g of a solution of $Cr(acac)_3$ in cyclohexane (60.52 ppm Cr) and 0.10880 g of a solution of $Co(EH)_2$ in cyclohexane (149 ppm Co) was placed in the same reactor as comparative example A. In the present example the chromium and cobalt concentrations used were 0.47 ppm and 0.07 ppm in the CH_x feed, respectively, giving a molar ratio of 0.13. The reaction was carried out using the same conditions and in the same way as in Comparative Example A.

Example 2

A mixture of 96.02 g of CH_x feed, 1.0041 g of biphenyl (internal standard), 0.6913 g of a solution of $Cr(acac)_3$ in cyclohexane (60.52 ppm Cr) and 0.16721 g of a solution of $Co(EH)_2$ in cyclohexane (149 ppm Co) was placed in the same reactor as comparative example A. In the present example the chromium and cobalt concentrations used were 0.44 ppm and 0.26 ppm in the CH_x feed, respectively, giving a molar ratio of 0.52. The reaction was carried out using the same conditions and in the same way as in Comparative Example A.

Example 3

A mixture of 101.02 g of CH_x feed, 1.4460 g of biphenyl (internal standard), 1.10698 g of a solution of $Cr(acac)_3$ in cyclohexane (60.52 ppm Cr) and 0.0629 g of a solution of $Co(EH)_2$ in cyclohexane (149 ppm Co) was placed in the same reactor as comparative example A. In the present example the chromium and cobalt concentrations used were 0.66 ppm and 0.09 ppm in the CH_x feed, respectively, giving a molar ratio of 0.12. The reaction was carried out using the same conditions and in the same way as in Comparative Example A.

Example 4

A mixture of 97.82 g of CH_x feed, 0.9932 g of biphenyl (internal standard), 1.10045 g of a solution of $Cr(acac)_3$ in cyclohexane (60.52 ppm Cr) and 0.09878 g of a solution of $Co(EH)_2$ in cyclohexane (149 ppm Co) was placed in the same reactor as comparative example A. In the present example the chromium and cobalt concentrations used were 0.68 ppm and 0.15 ppm in the CH_x feed, respectively, giving a molar ratio of 0.19. The reaction was carried out using the same conditions and in the same way as in Comparative Example A.

Example 5

A mixture of 96.00 g of CH_x feed, 1.0330 g of biphenyl (internal standard), 1.0675 g of a solution of $Cr(acac)_3$ in cyclohexane (60.52 ppm Cr) and 0.06899 g of a solution of $Co(EH)_2$ in cyclohexane (149 ppm Co) was placed in the same reactor as comparative example A. In the present example the chromium and cobalt concentrations used were 0.67 ppm and 0.10 ppm in the CH_x feed, respectively, giving a molar ratio of 0.13. The reaction was carried out using the same conditions and in the same way as in Comparative Example A.

Example 6

A mixture of 93.70 g of CH_x feed, 1.0192 g of biphenyl (internal standard), 0.7500 g of a solution of $Cr(acac)_3$ in cyclohexane (60.52 ppm Cr) and 0.01931 g of a solution of $Co(EH)_2$ in cyclohexane (149 ppm Co) was placed in the same reactor as comparative example A. In the present example the chromium and cobalt concentrations used were 0.48 ppm and 0.03 ppm in the CH_x feed, respectively, giving a molar ratio of 0.06. The reaction was carried out using the same conditions and in the same way as in Comparative Example A.

Example 7

A mixture of 95.73 g of CH_x feed, 0.9900 g of biphenyl (internal standard), 1.13181 g of a solution of $Cr(acac)_3$ in cyclohexane (60.52 ppm Cr) and 0.0236 g of a solution of $Co(EH)_2$ in cyclohexane (149 ppm Co) was placed in the same reactor as comparative example A. In the present example the chromium and cobalt concentrations used were 0.72 ppm and 0.04 ppm in the CH_x feed, respectively, giving a molar ratio of 0.05. The reaction was carried out using the same conditions and in the same way as in Comparative Example A.

In all Comparative Examples and Examples mentioned above, the main products analysed and included for the determination of conversion and selectivity were:

Cyclohexylhydroperoxide (CHHP)
Cyclohexanone
Cyclohexanol
Adipic acid
Hydroxycaproic acid
Caproic acid
Valeric acid
Butyric acid
Pentanol
Butanol
Caprolactone
Formic acid
CO
CO_2

The results obtained with the Examples and Comparative Examples above are provided in Tables 1-3 below for three different conversion levels (3, 4, and 5 mol%, as obtained by interpolation from the available series of experimental data). All results at the 5 mol% conversion level are comparative results.

Table 1. Results for conversion of 3 mol%

Example	[Co] (ppm in CHx feed)	[Cr] (ppm in CHx feed)	Atomic Co/Cr ratio	([Co] + [Cr]) (ppm in CHx feed)	Selectivity to CHHP + cyclohexanol + cyclohexanone (mol%)	Molar K/A ratio
Comp.Ex. A	/	0.43	0	0.43	85.12	1.72
Comp.Ex. B	/	0.86	0	0.86	85.07	1.53
Comp.Ex. C	1.02	0.88	1.02	1.9	84.73	1.38
Comp.Ex. D	1.04	0.57	1.60	1.61	87.63	1.02
Comp.Ex. E	0.25	/	/	0.25	88.11	0.54
Comp.Ex. F	0.50	/	/	0.50	87.05	0.59
Comp.Ex. G	0.27	0.75	0.32	1.02	85.25	1.34
Comp.Ex. H	0.31	0.65	0.42	0.96	84.89	1.26
Comp.Ex. I	1.00	4.40	0.20	5.40	83.60	1.00
Ex. 1	0.07	0.47	0.13	0.54	87.72	1.36
Ex. 2	0.26	0.44	0.52	0.70	86.80	1.38
Ex. 3	0.09	0.66	0.12	0.75	87.17	1.43
Ex. 4	0.15	0.68	0.19	0.83	86.37	1.32
Ex. 5	0.10	0.67	0.13	0.77	86.64	1.38
Ex. 6	0.04	0.48	0.07	0.51	86.21	1.36
Ex. 7	0.04	0.72	0.05	0.76	86.12	1.30

Table 2. Results for conversion of 4 mol%

Example	[Co] (ppm in CHx feed)	[Cr] (ppm in CHx feed)	Atomic Co/Cr ratio	([Co] + [Cr]) (ppm in CHx reed)	Selectivity to CHHP + cyclohexanol + cyclohexanone (mol%)	Molar K/A ratio
Comp.Ex. A	/	0.43	0	0.43	83.53	1.60
Comp.Ex. B	/	0.86	0	0.86	83.71	1.49
Comp.Ex. C	1.02	0.88	1.02	1.9	84.73	1.36
Comp.Ex. D	1.04	0.57	1.60	1.61	85.75	0.90
Comp.Ex. E	0.25	/	/	0.25	86.6	0.56
Comp.Ex. F	0.50	/	/	0.50	85.68	0.61
Comp.Ex. G	0.27	0.75	0.32	1.02	84.53	1.34
Comp.Ex. H	0.31	0.65	0.42	0.96	84.13	1.26
Comp.Ex. I	1.00	4.40	0.20	5.40	82.60	1.09
Ex. 1	0.07	0.47	0.13	0.54	85.87	1.24
Ex. 2	0.26	0.44	0.52	0.70	85.63	1.32
Ex. 3	0.09	0.66	0.12	0.75	85.86	1.42
Ex. 4	0.15	0.68	0.19	0.83	85.44	1.31
Ex. 5	0.10	0.67	0.13	0.77	85.74	1.35
Ex. 6	0.04	0.48	0.07	0.51	85.21	1.26
Ex. 7	0.04	0.72	0.05	0.76	85.45	1.31

Table 3. Results (all comparative) for conversion of 5 mol%

Example	[Co] (ppm in CHx feed)	[Cr] (ppm in CHx feed)	Atomic Co/Cr ratio	([Co] + [Cr]) (ppm in CHx feed)	Selectivity to CHHP + cyclohexanol + cyclohexanone (mol%)	Molar K/A ratio
Comp.Ex. A	/	0.43	0	0.43	81.83	1.46
Comp.Ex. B	/	0.86	0	0.86	82.33	1.43
Comp.Ex. C	1.02	0.88	1.02	1.9	82.39	1.33
Comp.Ex. D	1.04	0.57	1.60	1.61	83.50	0.81
Comp.Ex. E	0.25	/	/	0.25	84.98	0.57
Comp.Ex. F	0.50	/	/	0.50	84.21	0.62
Comp.Ex. G	0.27	0.75	0.32	1.02	83.82	1.31
Comp.Ex. H	0.31	0.65	0.42	0.96	83.08	1.24
Comp.Ex. I	1.00	4.40	0.20	5.40	81.83	1.12
Ex. 1	0.07	0.47	0.13	0.54	83.96	1.12
Ex. 2	0.26	0.44	0.52	0.70	84.23	1.22
Ex. 3	0.09	0.66	0.12	0.75	84.76	1.38
Ex. 4	0.15	0.68	0.19	0.83	84.30	1.27
Ex. 5	0.10	0.67	0.13	0.77	84.50	1.27
Ex. 6	0.04	0.48	0.07	0.51	83.72	1.17
Ex. 7	0.04	0.72	0.05	0.76	84.56	1.29

CLAIMS

1. Method for preparing a mixture comprising cyclohexanol and cyclohexanone in a molar cyclohexanone/cyclohexanol ratio of at least 1.2 and with a cyclohexane conversion of below 5 mol%, comprising oxidising cyclohexane in a liquid phase, said oxidising being catalysed by a cobalt compound and a chromium compound, wherein the atomic cobalt to chromium ratio is in the range of 0.05-0.8, and wherein the sum of the concentrations of cobalt and chromium is 0.05-0.9 ppm by weight based on the total weight of the reaction mixture, and wherein the cobalt compound and chromium compound are dissolved in the liquid phase.
2. Method according to claim 1, wherein the cobalt compound comprises at least one ligand selected from the group of acetylacetonates, octanoates, naphthenates, bipyridines, porphyrinates, and phthalocyanates.
3. Method according to claim 1 or 2, wherein the chromium compound comprises at least one ligand selected from the group of acetylacetonates, octanoates, naphthenates, bipyridines, porphyrinates, and phthalocyanates.
4. Method according to any one of the preceding claims, wherein the atomic cobalt to chromium ratio is in the range of 0.1-0.5, in particular in the range of 0.15-0.35.
5. Method according to any one of the preceding claims, wherein the sum of the concentrations of cobalt and chromium is 0.1-0.7 ppm by weight based on the total weight of the reaction mixture, in particular 0.2-0.6 ppm by weight.
6. Method according to any one of the preceding claims, wherein the cobalt concentration is 0.01-0.4 ppm by weight based on the total weight of the reaction mixture, in particular 0.05-0.2 ppm by weight.
7. Method according to any one of the preceding claims, wherein the chromium concentration is 0.04-0.8 ppm by weight based on the total weight of the reaction mixture, in particular 0.1-0.5 ppm by weight.
8. Method according to any one of the preceding claims, wherein the cyclohexane conversion is 2.5-4.5 mol%, in particular 3-4 mol%.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/066919

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C45/33 C07C49/403 C07C29/50 C07C35/08
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 598 869 A (VOLPE PETER J ET AL) 10 August 1971 (1971-08-10) cited in the application claim 5 -----	1-8
A	DATABASE WPI Week 198313 Thomson Scientific, London, GB; AN 1983-31424K XP002528835 & SU 929 213 A1 (GRODNO AZOT) 23 May 1982 (1982-05-23) cited in the application abstract -----	1-8

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
31 March 2010	12/04/2010

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2009/066919

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3598869 A	10-08-1971	NONE	
SU 929213 A1	23-05-1982	NONE	