Title: METHOD FOR THE CATALYZED DECOMPOSITION OF ORGANIC HYDROPEROXIDES

Abstract

The invention relates to an improvement in carrying out a catalyzed decomposition of organic hydroperoxides. The improvement consists in the use of a heterogeneous catalyst which is composed of a three-dimensional microporous structure, a so-called molecular sieve, containing aluminum, silicon and/or phosphorus oxides and a metal (Me) catalyst incorporated into the lattice. This catalyst yields substantially no loss in use, so that a considerable saving is achieved and moreover detriment to the environment through metal waste is avoided.
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Title: Method for the catalyzed decomposition of organic hydroperoxides.

The invention relates to a method for the catalyzed decomposition of organic hydroperoxides. Organic hydroperoxides are important intermediates in the preparation of, in particular, alcohols, ketones and acids, which in turn are frequently used as starting materials for organic synthesis processes.

A very important organic hydroperoxide is cyclohexyl-hydroperoxide (Chhp); which is obtained by oxidation of cyclohexane (Ch), and from which cyclohexanone (Chon) and cyclohexanol (Chol) are prepared through catalyzed decomposition. Chon can be converted to adipic acid, which is a reagent in the preparation of nylon 6.6. According to another industrial process, Chon is converted with hydroxylamine to form Chon-oxime, which, via a Beckmann transformation, yields ε-caprolactam, which is polymerized to nylon 6. The decomposition of Chhp takes place under the catalytic action of metals, in particular transition metals such as cobalt, according to a mechanism known under the name of Haber-Weiss mechanism. Much research has been devoted to the decomposition of Chhp, as appears from the numerous publications dealing with it. By way of illustration, reference may be made to J. Am. Chem. Soc. 1985, 107, 3534-3540, to Journal of Molecular Catalysis, 48 (1988) 129-148 and to an article by G.F. Pustarnakova, V.M. Solyanikov and E.T. Denisov, "Decomposition of Cyclohexyl Hydroperoxide under the Action of Chromium and Molybdenum Compounds", Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, pp. 547-552, March 1975. According to these publications, the catalytically active metals are used as an organic salt, for instance cobalt octoate, or in the form of a complex, but the catalysis involved is always a homogeneous catalysis, which means that the catalyst is present in dissolved condition, either in the organic liquid phase in which the
decomposition occurs, or in an aqueous phase which is in contact therewith. In all of the industrial processes for the decomposition of Chhp, too, homogeneous catalysis is employed.

The decomposition of Chhp using a homogeneous catalyst has a number of important disadvantages. The fact is it is inevitable that through lixiviation important quantities of catalyst are lost, ending up partly in the desired product and partly in waste streams. It is difficult to recover the catalyst therefrom, so that, on the one hand, fresh catalyst must always be added and, on the other, the environment is undesirably affected with metal waste coming from the lost catalyst. In addition, the selectivity in the known decomposition of Chhp with a homogeneous catalyst is rather unfavorable in the sense that, in addition to the desired Chon, approximately twice that amount of Chol is obtained, which must subsequently be converted to Chon by dehydrogenation.

EP-A-0 096 798 discloses the preparation of Chon and Chol by treating Chhp with a catalyst consisting of cobalt oxide deposited on a support from zeolite. This catalyst possesses a slight stability, so that important quantities of the catalytically active material are lost during use.

From EP-A-0 492 807 it is known to decompose all kinds of hydroperoxides, but particularly cumene hydroperoxide, under the catalytic activity of solid acid zeolites, preferably crystalline Y-zeolites modified by ion exchange with rare earth metals, such as lanthanum, or with metals from group VIII such as cobalt or nickel. Here, too, the catalytically active metal is insufficiently strongly bonded to the support material, so that it becomes easily detached in use. This publication, incidentally, is concerned with acid catalysis, more particularly the preparation of phenol and acetone from cumene hydroperoxide, while the invention relates to decompositions of the redox type, where no acid catalyst but a redox catalyst is used.
The object of the invention is to prevent the above-described loss of catalyst and thereby to avoid the environment being burdened with metal waste.

This object is achieved, in accordance with the invention, by carrying out the catalyzed decomposition of organic hydroperoxides utilizing a heterogeneous catalyst which is composed of a three-dimensional microporous structure, a so-called molecular sieve, comprising aluminum, silicon and/or phosphorus oxides and a metal (Me) catalyst incorporated into the lattice.

EP-A-0 203 632 describes a catalyst where aluminum and boron are incorporated into the lattice of zeolite crystals. This is an acid catalyst which is used in carrying out a specific acid catalysis. The fact is it has been found to effect a selective decomposition of cumene hydroperoxide in phenol and acetone.

The catalytic metal component (Me) of the present heterogeneous catalyst appears to remain inseparably bonded to the molecular sieve functioning as support, so that no metal (Me) is released into the reaction medium and also no metal (Me) is lost when the catalyst, for instance through filtration, is separated from the reaction medium and is subsequently reactivated to be used again.

Further, high conversion values have been observed when the present heterogeneous catalysts are used, which points to a high catalytic activity, while further a remarkably favorable selectivity could be established. In the decomposition of Chhp to form Chon and Chol, Chon/Chol ratios between approximately 50/50 and 90/10 were obtained, which is very favorable in comparison with Chon/Chol ratios between 30/70 and 35/65, which are achieved with homogeneous catalysis on industrial scale.

The heterogeneous catalysts to be used in accordance with the invention are composed of a molecular sieve in which catalytically active metals (Me) are incorporated, so that these constitute a fixed component of the molecular sieve. Molecular
sieves are inorganic crystalline solid substances which are provided with fine holes or cavities where reactions can take place. Examples of molecular sieves to be used in accordance with the invention include aluminophosphates (APOs), aluminophosphosilicates (SAPOs), aluminosilicates (zeolites) and silicalites (based exclusively on silica). On account of the metals (Me) incorporated into the crystal lattice in the preparation, such molecular sieves which are eligible for use in accordance with the invention can conveniently be designated as Me-APOs, Me-SAPOs, Me-zeolites and Me-silicalites.

The molecular sieves for use in accordance with the invention can be prepared by techniques which are known per se. These techniques have frequently been described in the literature, as will appear from the references specified hereinafter. In broad outline, the preparation can thus be carried out that first an aqueous paste is formed which contains the selected starting materials in the desired relative proportions. Suitable starting materials include hydrated aluminum oxide, hydrated silicon oxide, a source of phosphate ions, a source of ions of the selected metal (Me), typically a suitable Me-salt, and a so-called template, which is a compound which determines the positions where later the holes or cavities of the molecular sieve are formed. From the paste, typically via a gel structure, the intended crystalline structure of the molecular sieves is obtained. The metal (Me) then appears to be incorporated into the crystal lattice and occupy positions there which would otherwise be occupied by aluminum or silicon for instance. The ultimate heterogeneous catalyst is then obtained by calcination, whereby the organic template material is burnt from the holes or cavities.

The catalytic metal (Me) is selected from the transition metals from the groups IV A (Ti, etc.), V A (V, etc.), VI A (Cr, etc.), VII A (Mn, etc.) and VIII A (Fe, Co, Ni, etc.) of the Periodic System and the rare earth metals such as Ce, La, etc.
Typically, the metals involved are redox metals or metals which can occur in different valence states and in fact the same metals (Me) are eligible as can also be used in the homogeneous catalysis mentioned above. Which metal (Me) or which combination of metals (Me) is selected depends on the organic hydroperoxide it is desired to decompose and can easily be determined by a person of ordinary skill on the basis of simple experiments. It has for instance been found that in the decomposition of Chhp especially chromium and vanadium yield a particularly high efficiency along with a favorable selectivity to Chon relative to Chol. Cobalt and manganese also yield a favorable selectivity in the decomposition of Chhp.

In general, a better efficiency is attained according as more metal (Me) is incorporated into the molecular sieve.

However, practical limitations apply, because if the percentage of metal (Me) is too high, the metal cannot be permanently incorporated into the molecular sieve, so that during use release or lixiviation of Me occurs, which would be detrimental to the main object of the invention. It has been found that an amount of catalytic metal (Me) of from 0.5 to 4 and preferably of from 1 to 3 wt.%, based on the total catalyst, yields excellent results.

The holes or cavities in the molecular sieve should have a minimum size to allow the reaction medium and the reaction components present therein to penetrate. The minimum size is therefore mainly determined by the nature of the hydroperoxide to be decomposed, for instance Chhp, and the medium in which it is dissolved, for instance cyclohexane. Of course, larger holes or cavities may be present as well, but unduly large cavities, for instance of a size three or more times larger than the specified minimum size are less desirable, because they do not favor the efficient operation of the system. The desired size of the holes or cavities can be controlled in known manner, in particular by the choice of the template. Known and much used templates are organic cavity-forming or cavity-filling compounds, for instance
tri-alkylamines and tetra-alkylammonium salts, the size of the compounds used, for instance the length of the alkyl chains, being determinative of the final size of the holes or cavities. The actual holes or cavities are formed when the template is burnt away by an a final calcination.


The heterogeneous catalysts for use according to the invention are redox catalysts, which are different from acid catalysts, and are catalytically active in such a manner that, through decomposition of the hydroperoxide, reaction products are formed which can be situated along the redox line, such as the ketone and the alcohol which correspond with that hydroperoxide.

Organic hydroperoxides which can be decomposed in accordance with the present method can be represented by the general formula R'OOR, wherein R represents a primary, a secondary or a tertiary alkyl, alkenyl, alkynyl, cycloalkyl or aralkyl group, while the aromatic core may optionally be substituted by, for instance, alkyl, chlorine, etc. As examples of such hydroperoxides, the following compounds can be mentioned: cyclohexylhydroperoxide, cyclooctadecylhydroperoxide, ethylbenzenehydroperoxide, tetralinhydroperoxide, tert-butylhydroperoxide,
pinanehydroperoxide and isopropylbenzenehydroperoxide as well as
dihydroperoxides such as diisopropylbenzenedihydroperoxide.

For carrying out the present decomposition, in general the
same reaction conditions can be employed as in the known
decomposition of organic hydroperoxides with a homogeneous
catalyst. Typically, the starting-point is a 2-5% solution of the
hydroperoxide to be decomposed in a suitable solvent, preferably
in the hydrocarbon from which the hydroperoxide is made. Thus, in
the case of cyclohexylhydroperoxide, it is possible to start from
a 2-5% solution thereof in cyclohexane, for instance an
approximately 3% solution. To that solution the present
heterogeneous catalyst is added, whilst the amount of catalyst
can vary within wide limits. It is for instance possible to add
an amount of catalyst such that the molar ratio of hydroperoxide
to catalytic metal (Me) is in the range of 5/1 to 450/1. For
practical use on an industrial scale, such hydroperoxide to
catalytic metal (Me) ratio is preferably selected in the range of
10/1 to 250/1. The decomposition is then carried out by stirring
the reaction mixture at increased temperature, for instance at a
temperature of 50-80°C. These reaction conditions are known to a
person of ordinary skill or can easily be determined.

After the decomposition has been completed, the
heterogeneous catalyst is separated from the reaction mixture.
For this purpose, conventional techniques can be used, such as
filtration or centrifugation. Upon analysis of the reaction
product thus recovered, it appears that conversions of almost
100% can be achieved. This points to a high catalytic activity.
The fact that even at molar ratios of hydroperoxide to catalytic
metal (Me) of about 400/1 still a very reasonable conversion of
about 50% could be observed is a further indication of a high
catalytic activity. Further, upon analysis of the recovered
reaction product it also appears that a favorable selectivity can
be achieved. In fact, in the decomposition of Chhp, Chon/Chol
ratios of between approximately 50/50 and 90/10 were determined,
as mentioned hereinabove. Finally, no or practically no catalytic metal (Me) is found in the recovered reaction product, as could be established by an extremely sophisticated method of analysis, viz. by molecular spectrography of a sensitivity in the ppb range. Accordingly, no lixiviation of the catalytically active component, viz. the metal (Me), takes place.

The catalyst separated from the reaction mixture can be washed and reactivated. The reactivation is typically carried out by calcining the catalyst for some time. Then the catalyst can be used again. It appears to possess a high stability and even an increase of the catalytic activity could be observed. This constitutes supplementary evidence that the catalytically active metal (Me) is retained completely and that working in accordance with the invention prevents the environment from being damaged by the lost catalyst.

The invention will be further explained on the basis of a number of preparation instructions and examples.

1. Preparation of Cr–APO-5

55.1 ml demineralized water was added to 24.0 g pseudoboehmite (Pural SB, Condea Chemie) and the mixture was agitated for 2 minutes and subsequently stirred for 2 hours at room temperature.

4.6 g Cr₃(OH)₂(CH₃COO)₇ (Aldrich) was dissolved in 68.7 ml demineralized water and stirred at room temperature until the chromium salt was completely dissolved. The solution was then filtered to remove small amounts of insoluble residues. The solution obtained was combined with a solution of 51.2 g H₃PO₄ (85%; Baker) in 65.1 ml water.

The combined solution thus obtained was added to the paste of pseudoboehmite and was vigorously agitated, whereafter the homogeneous mixture was allowed to rest, for 1 hour under ambient conditions.
The mixture was cooled to 0°C with a bath of ice in water and 31.5 g tripropylamine (Janssen) was dropwise added with stirring at 0°C. Thus a gel was formed which was stirred at 0°C for 2 hours.

The viscous gel was placed in a teflon-coated 50 ml autoclave and heated in an oven for 24 h at 175°C under autogenous pressure. The autoclave was cooled with an air stream and the Cr-APO-5 crystals were recovered by stirring the contents of the autoclave for a few minutes in 300 ml demineralized water to allow the crystals to settle and decanting the supernatant liquid. This procedure was repeated a number of times until a clear liquid was obtained. Then 150 ml ethanol was used to wash the crystals twice. Then the crystals were filtered off and dried for 4 h at 120°C.

The calcination was carried out by heating the crystals to 480°C with a temperature increase of 60°C/hour and maintaining them at 480°C for 5 h.

The above described method of preparation deviates at some points from the preparation of Cr-APO-5 described in U.S Patent No. 4,759,919.

The molar composition of the Cr-APO-5 obtained is as follows:

\[ 0.05\text{Cr}_2\text{O}_3:0.9\text{Al}_2\text{O}_3:0.2\text{P}_2\text{O}_5:0.2\text{Pr}_3\text{N}:40\text{H}_2\text{O} \]

The Cr-APO-5 composition and structure were determined by the following techniques and by comparison with examples from the literature:

- X-ray powder diffraction patterns were measured on a Philips PW 1877 automatic powder diffractometer utilizing CuKα radiation (see the accompanying figure and a figure from the literature for comparison);
a sample coated with an Au film applied by vaporization was examined under a scanning electron microscope (SEM), for which a Jeol JSM-35 microscope was used;

diffuse reflection spectra (DRS) were measured with a Hitachi 150-20 UV-VIS spectrophotometer provided with a diffuse reflection unit; the spectra were measured at wavelengths of 190 to 900 nm;
elemental analysis of the calcined Me-APOs was performed by the use of inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkin-Elmer Plasma-II); the sample to be analyzed was pretreated as follows: 150 mg of the calcined Me-APO was weighed out in a plastics bottle and 6 ml of an acid solution prepared by diluting 1 ml concentrated H₂SO₄ with 4 ml water and 1 ml 40% HF was added to the bottle; the bottle was closed and stored for 4-6 h at 60°C; then the bottle was cooled with ice and 8 ml 2.5% H₃BO₃ was added; finally it was filled up with water to 100 ml.

2. Preparation of Co-APO-5

Co-APO-5 was prepared similarly to Cr-APO-5, but instead of Cr₃(OH)₂(CH₃COO)₇ an equimolar amount of CoSO₄·7H₂O (Janssen) was used. The composition and structure were determined by the above-mentioned techniques.

3. Preparation of Mn-APO-5

Mn-APO-5 was also prepared similarly to Cr-APO-5, but instead of Cr₃(OH)₂(CH₃COO)₇ an equimolar amount of Mn(CH₃COO)₂·4H₂O (Janssen) was used. The composition and structure were determined by the above-mentioned techniques.
4. Preparation of V-APO-11

8 ml demineralized water was added to 4.26 g pseudoboehmite (75 wt.% Al₂O₃) and the mixture was agitated for 2 h at room temperature. Then 9.3 g H₃PO₄ (85%; Merck) was dissolved therein and the liquid (A) obtained was stored at room temperature.

1.918 g vanadylsulfate (VOSO₄·5H₂O; Merck) was dissolved in 18 ml demineralized water, followed by stirring at room temperature until the vanadium salt was completely dissolved.

The vanadium solution was added to liquid (A), whereafter the mixture was cooled in a water/ice bath. Then 4.12 g diisopropylamine was dropwise added to the mixture with stirring. A gel was obtained, which was stirred for 2 h at a temperature between 0 and 5°C.

The viscous blue gel was charged to a teflon-coated 50 ml autoclave and heated in an oven at 175°C for 2 days under autogenous pressure.

The further steps are analogous to what is described in preparation 1.

The above-described method of preparation deviates at some points from the preparation of V-APO-11 described in U.S. Patent No. 4,310,440.

The V-APO-11 composition and structure were determined by the techniques mentioned at the end of preparation 1.

5. Preparation of V-APO-5
V-APO-5 was prepared in the same manner as V-APO-11, except that as template triethanolamine was used instead of diisopropylamine.

The determination of the composition and structure of V-APO-5, too, was carried out in the same manner as for V-APO-11.

6. Preparation of Cr-silicalite

A solution (A) was prepared of 0.54 g CrCl₃·6H₂O, 3.60 g NaCl, 1.72 g tetrapropylammonium bromide and 1.82 g H₂SO₄ (98%) in 17.35 g H₂O.

A solution (B) was prepared, consisting of 22.05 g Na₂SiO₃ in 14.5 g H₂O.

A solution (C) was prepared of 12.22 g NaCl, 0.66 g tetrapropylammonium bromide, 0.72 g NaOH and 0.60 g H₂SO₄ (98%) in 62 g H₂O.

The solutions (A) and (B) were slowly introduced into solution (C) with a supply pump, with stirring and under a nitrogen stream. The supply rate was regulated such that the pH of the mixture was kept within the range 10-10.5. The supply time was 20 minutes. Although some gel precipitation was observed, the solution was stirred for another 30 minutes. Then the solution was homogenized for 1 h. The solution was then transferred into an autoclave of stainless steel which was provided with a teflon coating.

In the autoclave the solution, with stirring (120 tpm) under autogenous pressure, was first heated to 150°C in 2 h and subsequently to 220°C in 3 h. The temperature was then maintained at 220°C for 3 h, followed by cooling.
The crystals thus formed were washed with water and dried in a vacuum oven overnight at 80°C. Then the crystals were calcined for one day at 550°C.

The H-form in the crystals was subjected to ion exchange with (NH₄)₂CO₃ and then calcined for 3 h at 470°C.

The composition and structure of the product obtained were confirmed on the basis of XRD spectra and by comparison with examples from the literature. Figures presenting the XRD of the product prepared and of an example from the literature for comparison are annexed. The product prepared possesses the so-called pentasil structure.

7. Preparation of Co-ZSM-5

Co-ZSM-5 was prepared in the manner as described by Joseph A. Rossin, Carlos Saldarriaga and Mark E. Davis, "Synthesis of cobalt containing ZSM-5", Zeolites, 1987, Vol. 7, pp. 295-300. A zeolite was prepared with a mole ratio Si/Al = 60. The product obtained was identified according to the methods of analysis indicated in the article in question.

Example 1

This example describes the catalytic decomposition of cyclohexylhydroperoxide (Chhp) utilizing heterogeneous catalysts according to the invention.

The reaction was carried in a 50 ml flask which was provided with a condensor and a magnetic agitator. 3.08 g of a Chhp-solution in cyclohexane (883 mmol Chhp/kg cyclohexane), 10 ml cyclohexane and an amount of heterogeneous catalyst corresponding
with 0.028 mmol catalytic metal (Me) were introduced into the flask. Then the flask was heated with circulating water of 70°C and stirred for 5 h. The reaction mixture was then cooled, whereafter the catalyst was separated by centrifugation.

The reaction solution thus obtained was analyzed to determine the selectivity and the conversion percentage.

The amounts of Chon and Chol were determined by gas chromatography analysis (GC). This was carried out under the following conditions: column 10 m x 0.53 mm, CP WAX 52 CB, film thickness 2.04 μm, ratio 65; temperature program 80°C, 0 min; 5°C/min; 140°C, 0 min. The sample to be analyzed was prepared as follows: to 10 ml of a triphenylphosphine solution in 1,2-dichloroethane (24 g/l) 15 μl hexadecane (internal standard) was added. 20 μl of the sample to be examined was added to 0.3 ml of the solution thus prepared. The solution thus obtained was agitated for a few seconds. Then 0.5 μl of this solution was analyzed directly by GC.

The conversion percentage was determined by titration of Chhp: to 35 ml chloroform/acetic acid (1:2 v/v) 3.0 g of the sample to be examined was added and then 2.5 ml of an aqueous KI solution (65 g/100 ml). The solution thus obtained was set in the dark for 0.5 h. After addition of 50 ml demineralized water, the solution was titrated with a 0.1 N solution of sodium thiosulfate until the brown-yellow color disappeared. A control sample containing no Chhp was analyzed as well.

The results of these tests, carried out utilizing heterogeneous catalysts of which the preparation instructions are specified above, are shown in Table 1 below.
Table 1

Decomposition of Chhp catalyzed by molecular sieves with metal substitution (Me)

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<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
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<td>chon</td>
<td>chol</td>
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<td>Cr-APO-5</td>
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<td>87</td>
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<tr>
<td>Cr-silicalite</td>
<td>98</td>
<td>64</td>
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<tr>
<td>V-APO-11</td>
<td>76</td>
<td>50</td>
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<td>V-APO-5</td>
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</tr>
<tr>
<td>Co-ZSM-5</td>
<td>24</td>
<td>43</td>
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From these results it appears that a high to very high conversion can be achieved, while the chon/chol ratio is favorable (43/50) to very favorable (87/13).

Finally, the reaction solution was also examined for traces of catalytic metal (Me) originating from the heterogeneous catalyst used. This examination was carried out through molecular spectrography. No traces of Me in the ppb range could be demonstrated. Accordingly, no release or lixiviation of the catalytic metal component (Me) occurs.

Example 2

Two of the heterogeneous catalysts used in Example 1 were recirculated, a first time without being reactivated, and subsequently after being reactivated through calcination. This last was carried out by washing the catalyst separated from the reaction mixture twice, each time with 40 ml cyclohexane,
followed by centrifugation. The catalyst was then dried in vacuo at 80°C for 3 h and then placed in an oven to be calcined. The catalyst was heated to 480°C with a temperature increase of 60°C/hour and then maintained at 480°C for 5 h.

The results of these tests are shown in Table 2 below.

Table 2

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<th>conversion (%)</th>
<th>selectivity (%)</th>
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<td>chon</td>
<td>chol</td>
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<td>Cr-APO-5</td>
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<td>Cr-silicalite</td>
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<td></td>
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<tr>
<td>1</td>
<td>97</td>
<td>66</td>
</tr>
<tr>
<td>2*</td>
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<tr>
<td>25</td>
<td>90</td>
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* without calcination prior to recirculation

From these results it appears that the conversion and the selectivity remain substantially the same. When the Cr-APO-5 catalyst is used, even an increase of the catalytic activity can be observed. This constitutes supplementary evidence that no catalytically active metal (Me) is lost, and hence no detriment to the environment is to be feared.
Example 3

The decomposition of Chhp described in Example 1 was repeated utilizing varying amounts of Cr-APO-5 catalyst. The results obtained are shown in Table 3 below.

Table 3

<table>
<thead>
<tr>
<th>mole ratio Cr/Chhp</th>
<th>conversion (%)</th>
<th>selectivity (%)</th>
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<tr>
<td></td>
<td>Chon</td>
<td>Chol</td>
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<tr>
<td>10</td>
<td>94</td>
<td>79 12</td>
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<td>15</td>
<td>91</td>
<td>86 13</td>
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<td>20</td>
<td>83</td>
<td>87 13</td>
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<tr>
<td>380</td>
<td>50</td>
<td>80 18</td>
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The results obtained demonstrate that even if only very small amounts of catalyst are used, still a reasonable conversion is obtained, so that the catalyst can be qualified as highly active. In addition, the selectivity remains very good at all times, regardless of the concentration of catalyst.
1. A method for the catalyzed decomposition of organic 
hydroperoxides, characterized in that said decomposition is 
5 carried out utilizing a heterogeneous catalyst which is composed 
of a three-dimensional microporous structure, a so-called 
molecular sieve, containing aluminum, silicon and/or phosphorus 
oxides and a metal (Me) catalyst incorporated into the lattice. 
2. A method according to claim 1, characterized in that the 
molecular sieve is an aluminophosphate (APO). 
3. A method according to claim 1, characterized in that the 
molecular sieve is an aluminophosphosilicate (SAPO). 
4. A method according to claim 1, characterized in that the 
molecular sieve is a silicalite. 
5. A method according to claim 1, characterized in that the 
molecular sieve is an aluminosilicate (zeolite). 
10 6. A method according to any one of claims 1-5, characterized 
in that the metal (Me) is selected from the groups V A (V, etc.), 
VI A (Cr, etc.) and VIII A (Co, etc.) of the Periodic System. 
7. A method according to claim 6, characterized in that the 
metal (Me) is chromium. 
15 8. A method according to claim 7, characterized in that the 
heterogeneous catalyst is Cr-APO-5. 
9. A method according to claim 7, characterized in that the 
heterogeneous catalyst is Cr-silicalite. 
10. A method according to any one of claims 1-9, characterized 
in that the catalyzed decomposition is a decomposition of the 
redox type.
11. A method according to claim 10, characterized in that the method is used for the catalyzed decomposition of cyclohexylhydroperoxide to form cyclohexanone and cyclohexanol.

12. A method according to any one of claims 1-11, characterized in that the heterogeneous catalyst is separated from the reaction medium, is reactivated by calcination and is used again for the catalyzed decomposition of organic hydroperoxides.
Fig. X-ray powder diffraction pattern of calcined Cr-silicalite in literature.

Fig. X-ray powder diffraction pattern of calcined Cr-silicalite.
Fig. X-ray powder diffraction pattern of AlPO₄-5 in literature.

Fig. X-ray powder diffraction pattern of calcined CrAPO-5.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C07C45/53 C07C49/403 C07C29/132 C07C35/08

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)
IPC 5 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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<th>Relevant to claim No.</th>
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<td>EP,A,0 492 807 (TEXACO CHEMICAL COMPANY) 1 July 1992 see page 4, line 25 - line 28; claim 1</td>
<td>1,5</td>
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<td>EP,A,0 203 632 (ENICHEM SINTESI S.P.A.) 3 December 1986 see claim 1</td>
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<td>A</td>
<td>EP,A,0 096 798 (BASF AKTIENGESELLSCHAFT) 28 December 1983 see claims</td>
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents:
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"&" document member of the same patent family

Date of the actual completion of the international search: 4 January 1994

Date of mailing of the international search report: 12. 01. 94

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HU Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016

Authorized officer
Bonneville, E
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