



TITLE
HYDROPEROXIDE DECOMPOSITION PROCESS
FIELD OF THE INVENTION

The invention generally relates to an improved catalytic process for
5 decomposing alkyl or aromatic hydroperoxides to form a mixture containing the
corresponding alcohol and ketone. In particular, the invention relates to
decomposing a hydroperoxide by contacting it with a catalytic amount of a
heterogenous catalyst comprised of gold, wherein one or more additional metals
selected from Periodic Group VIII is/are also present with gold.

10 BACKGROUND OF THE INVENTION

Industrial processes for the production of mixtures of cyclohexanol and
cyclohexanone from cyclohexane are currently of considerable commercial
significance and are well described in the patent literature. In accordance with
typical industrial practice, cyclohexane is oxidized to form a reaction mixture
15 containing cyclohexyl hydroperoxide (CHHP). The resulting CHHP is
decomposed, optionally in the presence of a catalyst, to form a reaction mixture
containing cyclohexanol and cyclohexanone. In the industry, such a mixture is
known as a K/A (ketone/alcohol) mixture, and can be readily oxidized to produce
adipic acid, which is an important reactant in processes for preparing certain
20 condensation polymers, notably polyamides. Due to the large volumes of adipic
acid consumed in these and other processes, improvements in processes for
producing adipic acid and its precursors can be used to provide beneficial cost
advantages.

Druliner et al., U.S. Patent No. 4,326,084, disclose an improved catalytic
25 process for oxidizing cyclohexane to form a reaction mixture containing CHHP,
and for subsequently decomposing the resulting CHHP to form a mixture
containing K and A. The improvement involves the use of certain transition metal
complexes of 1,3-bis(2-pyridylimino)isoindolines as catalysts for cyclohexane
oxidation and CHHP decomposition. According to this patent, these catalysts
30 demonstrate longer catalyst life, higher CHHP conversion to K and A, operability
at lower temperatures (80-160°C), and reduced formation of insoluble metal-
containing solids, relative to results obtained with certain cobalt(II) fatty acid
salts, e.g., cobalt 2-ethylhexanoate.

Druliner et al., U.S. Patent No. 4,503,257, disclose another improved
35 catalytic process for oxidizing cyclohexane to form a reaction mixture containing
CHHP, and for subsequently decomposing the resulting CHHP to form a mixture
containing K and A. This improvement involves the use of Co_3O_4 , MnO_2 , or
 Fe_3O_4 applied to a suitable solid support as catalysts for cyclohexane oxidation



29 September 2003

and CHHP decomposition at a temperature from about 80°C to about 130°C, in the presence of molecular oxygen.

5 Sanderson et al., U.S. Patent No. 5,414,163, disclose a process for preparing t-butyl alcohol from t-butyl hydroperoxide in the liquid phase over catalytically effective amounts of titania, zirconia, or mixtures thereof.

Sanderson et al., U.S. Patent Nos. 5,414,141, 5,399,794 and 5,401,889, disclose a process for preparing t-butyl alcohol from t-butyl hydroperoxide in the liquid phase over catalytically effective amounts of palladium with gold as a dispersing agent supported on alumina.

10 Druliner et al., U.S. provisional application 60/025,368 filed September 3, 1996 (now PCT US97/15332 filed September 2, 1997), disclose decomposing a hydroperoxide by contacting it with a catalytic amount of a heterogenous catalyst of Zr, Nb, Hf and Ti hydroxides or oxides. Preferably, the catalyst is supported on SiO₂, Al₂O₃, carbon or TiO₂. Alumina is a preferred support.

15 WO A-98/34894 discloses a process for decomposing hypoperoxides to their corresponding alcohol and ketone.

Further improvements and options are needed for hydroperoxide decomposition to K/A mixtures in order to overcome the deficiencies inherent in the prior art. Other objects and advantages of the present invention will become
20 apparent to those skilled in the art upon reference to the detailed description which hereinafter follows.

SUMMARY OF THE INVENTION

In accordance with the present invention, an improved process is provided in which a hydroperoxide is decomposed to form a decomposition reaction
25 mixture containing a corresponding alcohol and ketone. The improvement comprises decomposing hydroperoxide by contacting a hydroperoxide with a catalytic amount of a catalytic amount of a heterogenous catalyst comprised of gold, wherein one or more additional metals selected from Periodic Group VIII is/are also present with gold. Moreover, the catalysts are optionally supported on
30 a suitable support member, such as SiO₂, Al₂O₃, carbon, zirconia, MgO or TiO₂.

Preferably the additional metal is Pt or Pd. The process may optionally be run in the presence of hydrogen gas.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

35 The present invention provides an improved process for conducting a hydroperoxide decomposition step in an industrial process in which an alkyl or aromatic compound is oxidized to form a mixture of the corresponding alcohol and ketone. In particular, cyclohexane can be oxidized to form a mixture containing cyclohexanol (A) and cyclohexanone (K). The industrial process

29 September 2003

involves two steps: first, cyclohexane is oxidized, forming a reaction mixture containing CHHP; second, CHHP is decomposed, forming a mixture containing K

and A. As previously mentioned, processes for the oxidation of cyclohexane are well known in the literature and available to those skilled in the art.

Advantages of the present heterogenous catalytic process, relative to processes employing homogenous metal catalysts, such as metal salts or metal/ligand mixtures, include longer catalyst life, improved yields of useful products, and the absence of soluble metal compounds.

The improved process can also be used for the decomposition of other alkane or aromatic hydroperoxides, for example, t-butyl hydroperoxide, cyclododecylhydroperoxide and cumene hydroperoxide.

The CHHP decomposition process can be performed under a wide variety of conditions and in a wide variety of solvents, including cyclohexane itself. Since CHHP is typically produced industrially as a solution in cyclohexane from catalytic oxidation of cyclohexane, a convenient and preferred solvent for the decomposition process of the invention is cyclohexane. Such a mixture can be used as received from the first step of the cyclohexane oxidation process or after some of the constituents have been removed by known processes such as distillation or aqueous extraction to remove carboxylic acids and other impurities.

The preferred concentration of CHHP in the CHHP decomposition feed mixture can range from about 0.5% by weight to 100% (i.e., neat). In the industrially practiced route, the preferred range is from about 0.5% to about 3% by weight.

Suitable reaction temperatures for the process of the invention range from about 80°C to about 170°C. Temperatures from about 110°C to about 130°C are typically preferred. Reaction pressures can preferably range from about 69 kPa to about 2760 kPa (10-400 psi) pressure, and pressures from about 276 kPa to about 1380 kPa (40-200 psi) are more preferred. Reaction time varies in inverse relation to reaction temperature, and typically ranges from about 2 to about 30 minutes.

As noted previously, the heterogenous catalysts of the invention include Au, Ag, Cu (including, but not limited to, Au, Ag and Cu sol-gel compounds) and certain non-Au/Ag/Cu sol-gel compounds, preferably applied to suitable solid supports. The inventive process may also be performed using Au, Ag or Cu in the presence of other metals (e.g., Pd). The metal to support percentage can vary from about 0.01 to about 50 percent by weight, and is preferably about 0.1 to about 10 wt. percent. Suitable, presently preferred supports include SiO₂ (silica), Al₂O₃ (alumina), C (carbon), TiO₂ (titania), MgO (magnesia) or ZrO₂ (zirconia). Zirconia and alumina are particularly preferred supports, and Au supported on alumina is a particularly preferred catalyst of the invention.

Some of the heterogenous catalysts of the invention can be obtained already prepared from manufacturers, or they can be prepared from suitable starting materials using methods known in the art. These methods can include sol-gel techniques as described in more detail below for preparing both Au/Ag/Cu
5 sol-gel compounds and other non-Au/Ag/Cu sol-gel compounds. Supported gold catalysts can be prepared by any standard procedure known to give well-dispersed gold, such as evaporative techniques or coatings from colloidal dispersions.

In particular, ultra-fine particle sized gold is preferred. Such small particulate gold (often smaller than 10nm) can be prepared according to Haruta,
10 M., "Size-and Support-Dependency in the Catalysis of Gold", Catalysis Today 36 (1997) 153-166 and Tsubota et al., Preparation of Catalysts V, pp. 695-704 (1991). Such gold preparations produce samples that are purple-pink in color instead of the typical bronze color associated with gold and result in highly dispersed gold catalysts when placed on a suitable support member. These highly
15 dispersed gold particles typically are from about 3 nm to about 15 nm in diameter.

The catalyst solid support, including SiO_2 , Al_2O_3 , carbon, MgO , zirconia, or TiO_2 , can be amorphous or crystalline, or a mixture of amorphous and crystalline forms. Selection of an optimal average particle size for the catalyst supports will depend upon such process parameters as reactor residence time and
20 desired reactor flow rates. Generally, the average particle size selected will vary from about 0.005 mm to about 5 mm. Catalysts having a surface area larger than $10 \text{ m}^2/\text{g}$ are preferred since increased surface area of the catalyst has a direct correlation with increased decomposition rates in batch experiments. Supports having much larger surface areas can also be employed, but inherent brittleness of
25 high-surface area catalysts, and attendant problems in maintaining an acceptable particle size distribution, will establish a practical upper limit upon catalyst support surface area. A preferred support is alumina; more preferred is α -alumina and γ alumina.

A "sol-gel technique" is a process wherein a free flowing fluid solution,
30 "sol", is first prepared by dissolving suitable precursor materials such as colloids, alkoxides or metal salts in a solvent. The "sol" is then dosed with a reagent to initiate reactive polymerization of the precursor. A typical example is tetraethoxyorthosilicate (TEOS) dissolved in ethanol. Water, with trace acid or base as catalyst to initiate hydrolysis, is added. As polymerization and
35 crosslinking proceeds, the free flowing "sol" increases in viscosity and can eventually set to a rigid "gel". The "gel" consists of a crosslinked network of the desired material which encapsulates the original solvent within its open porous structure. The "gel" may then be dried, typically by either simple heating in a

flow of dry air to produce a xerogel or the entrapped solvent may be removed by displacement with a supercritical fluid such as liquid CO₂ to produce an aerogel. These aerogels and xerogels may be optionally calcined at elevated temperatures (>200°C) which results in products which typically have very porous structures and concomitantly high surface areas.

In practice of the invention, the catalysts can be contacted with CHHP by formulation into a catalyst bed, which is arranged to provide intimate contact between catalysts and reactants. Alternatively, catalysts can be slurried with reaction mixtures using techniques known in the art. The process of the invention is suitable for batch or for continuous CHHP decomposition processes. These processes can be performed under a wide variety of conditions.

Adding air or a mixture of air and inert gases to CHHP decomposition mixtures provides higher conversions of process reactants to K and A, since some cyclohexane is oxidized directly to K and A, in addition to K and A being formed by CHHP decomposition. This ancillary process is known as "cyclohexane participation", and is described in detail in Druliner et al., U.S. Patent No. 4,326,084, the entire contents of which are incorporated by reference herein. Other gases may also be added or co-fed to the reaction mixture as needed. Inert gases such as nitrogen may also be added to the reaction alone or in combination with other gases.

The results of the CHHP decomposition reaction, such as the K/A ratio or conversion rate, can be adjusted by choice of catalyst support, gases added to the reaction mixture, or metals added to the heterogeneous catalysts of the invention.

Preferably, metals added to the heterogeneous catalysts of the invention are for use as promoters, synergist additives, or co-catalysts are selected from Periodic Group VIII, hereby defined as Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, and Pt. Most preferred is Pd and Pt.

One preferred gas that can be added to the reaction mixture is hydrogen. An advantage of the addition of hydrogen is that the K/A ratio can be varied according to need. The addition of hydrogen can also convert impurities or by-products of the reactions, such as benzene, to more desirable products.

The process of the present invention is further illustrated by the following non-limiting examples. In the examples, all temperatures are in degrees Celsius and all percentages are by weight unless otherwise indicated.

EXPERIMENTS

Experiment 1 ~1.4% Au on Carbon

5 g of 20-35 mesh (0.5-0.85 mm) charcoal carbon (EM Science, Cherry Hill, NJ) was calcined in flowing helium (100 mL/min) at 400°C for 1 hour. This

material was then slurried into a solution of 0.1 g gold trichloride in 10 mL water containing 1 mL concentrated HCl. The slurry was stirred for 15 minutes at room temperature and then evaporated to dryness on a rotary evaporator. The recovered solid was calcined in flowing nitrogen (100 mL/min) at 400°C for 1 hour, cooled and then stored in tightly capped vial for testing as a CHHP decomposition catalyst.

Experiment 2 ~1.4% Au on Silica

5 g of + 8 mesh silica gel with surface area 300 m²/g and pore volume 1 cc/g (Alfa Aesar, Ward Hill, MA) was calcined in flowing helium (100 mL/min) at 400°C for 1 hour. This material was then slurried into a solution of 0.1 g gold trichloride in 10 mL water containing 1 mL concentrated HCl. The slurry was stirred for 15 minutes at room temperature and then evaporated to dryness on a rotary evaporator. The recovered solid was calcined in flowing nitrogen (100 mL/min) at 400°C for 1 hour, cooled and then stored in tightly capped vial for testing as a CHHP decomposition catalyst.

Experiment 3 ~14% Au on Silica

5 g of <2 micron silica gel with surface area 450 m²/g and pore volume 1.6 cc/g (Alfa Aesar, Ward Hill, MA) was calcined in flowing helium (100 mL/min) at 400°C for 1 hour. This material was then slurried into a solution of 1.0 g gold trichloride in 10 mL water containing 1 mL concentrated HCl. The slurry was stirred for 15 minutes at room temperature and then evaporated to dryness on a rotary evaporator. The recovered solid was calcined in flowing nitrogen (100 mL/min) at 400°C for 1 hour, cooled and then stored in tightly capped vial for testing as a CHHP decomposition catalyst.

Experiment 4 - Plain Silica Control

5 g of + 8 mesh silica gel with surface area 300 m²/g and pore volume 1 cc/g (Alfa Aesar, Ward Hill, MA) was calcined in flowing helium (100 mL/min) at 400°C for 1 hour. This material was then slurried into a solution of 10 mL water containing 1 mL concentrated HCl. The slurry was stirred for 15 minutes at room temperature and then evaporated to dryness on a rotary evaporator. The recovered solid was calcined in flowing nitrogen (100 mL/min) at 400°C for 1 hour, cooled and then stored in tightly capped vial for testing as a CHHP decomposition catalyst.

Experiment 5 ~1.4% Au on α -Alumina

5 g of 6-12 mesh α -alumina spheres (Calsicat, Erie, PA) was slurried into a solution of 0.1 g gold trichloride in 10 mL water containing 1 mL concentrated HCl. The slurry was stirred for 15 minutes at room temperature and then evaporated to dryness on a rotary evaporator. The recovered solid was calcined in

flowing nitrogen (100 mL/min) at 400°C for 1 hour, cooled and then stored in tightly capped vial for testing as a CHHP decomposition catalyst.

Experiment 6 ~13% Ag on Silica

5 g of + 8 mesh silica gel with surface area 300 m²/g and pore volume
5 1 cc/g (Alfa Aesar, Ward Hill, MA) was calcined in flowing helium (100 mL/min) at 400°C for 1 hour. This material was then slurried into a solution of 1.0 g silver nitrate in 10 mL water containing 1 mL concentrated HNO₃. The slurry was stirred for 15 minutes at room temperature and then evaporated to dryness on a rotary evaporator. The recovered solid was calcined in flowing nitrogen
10 (100 mL/min) at 400°C for 1 hour, cooled to 200°C and calcined another 1 hour in flowing hydrogen (100 mL/min) and then stored in tightly capped vial for testing as a CHHP decomposition catalyst.

Experiment 7 ~ 4.5% Cu on Silica

5 g of + 8 mesh silica gel with surface area 300 m²/g and pore volume
15 1 cc/g (Alfa Aesar, Ward Hill, MA) was calcined in flowing helium (100 mL/min) at 400°C for 1 hour. This material was then slurried into a solution of 1.0 g copper nitrate in 10 mL water containing 1 mL concentrated HNO₃. The slurry was stirred for 15 minutes at room temperature and then evaporated to dryness on a rotary evaporator. The recovered solid was calcined in flowing nitrogen
20 (100 mL/min) at 400°C for 1 hour, cooled to 200°C and calcined another 1 hour in flowing hydrogen (100 mL/min) and then stored in tightly capped vial for testing as a CHHP decomposition catalyst.

Unlike Experiments 1-7, Experiments 8-13 were carried out according to the general gold deposition technique of Tsubota et al., Preparation of Catalysts V, pp. 695-704 (1991) to produce ultra-fine gold particles. These supported catalysts
25 were purple/pink in color compared to the bronze/gold (higher loadings) or brown/grey (lower loadings) supported catalysts of Experiments 1-7.

Experiment 8 ~1% Au on MgO

10 g of powdered - 200 mesh MgO (Alfa Aesar, Ward Hill, MA) was
30 slurried into a solution of 0.2 g gold trichloride in 50 mL water containing 1 mL concentrated HCl. The pH of the slurry was adjusted to 9.6 with sodium carbonate solution and then 0.69 g sodium citrate was added. After stirring for 2 hours at room temperature the solid was recovered by filtration and washed well with distilled water. The recovered solid was calcined in flowing air
35 (100 mL/min) at 250°C for 5 hour, cooled and then stored in tightly capped vial for testing as a CHHP decomposition catalyst.

Experiment 9 ~1% Au on γ -Alumina

10 g of powdered - 60 mesh γ -alumina (Alfa Aesar, Ward Hill, MA) was slurried into a solution of 0.2 g gold trichloride in 50 mL water containing 1 mL concentrated HCl. The pH of the slurry was adjusted to 9.6 with sodium carbonate solution and then 0.69 g sodium citrate was added. After stirring for 2 hours at room temperature the solid was recovered by filtration and washed well with distilled water. The recovered solid was calcined in flowing air (100 mL/min) at 250°C for 5 hours, cooled and then stored in tightly capped vial for testing as a CHHP decomposition catalyst. The resulting catalyst was purple/pink in color and had a gold particle size of 8nm as determined by x-ray diffraction (XRD).

Experiment 10 ~1% Au on Silica

10 g of silica + 8 mesh granules (Alfa Aesar, Ward Hill, MA) was slurried into a solution of 0.2 g gold trichloride in 50 mL water containing 1 mL concentrated HCl. The pH of the slurry was adjusted to 9.6 with sodium carbonate solution and then 0.69 g sodium citrate was added. After stirring for 2 hours at room temperature the solid was recovered by filtration and washed well with distilled water. The recovered solid was calcined in flowing air (100 mL/min) at 250°C for 5 hours, cooled and then stored in tightly capped vial for testing as a CHHP decomposition catalyst.

Experiment 11 ~1% Au on Titania

10 g of powdered - 325 mesh titania (Alfa Aesar, Ward Hill, MA) was slurried into a solution of 0.2 g gold trichloride in 50 mL water containing 1 mL concentrated HCl. The pH of the slurry was adjusted to 7.0 with sodium carbonate solution and then 1.5 g sodium citrate was added. After stirring for 2 hours at room temperature the solid was recovered by filtration and washed well with distilled water. The recovered solid was calcined in flowing air (100 mL/min) at 400°C for 5 hours, cooled and then stored in tightly capped vial for testing as a CHHP decomposition catalyst.

Experiment 12 ~1% Au on Zirconia

10 g - 325 mesh zirconia (Calsicat #96F-88A, Erie, PA) was slurried into a solution of 0.2 g gold chloride in 50 mL water and 1 drop conc. HCl. The slurry was stirred gently as the pH was adjusted to 9.6 with 0.1M sodium carbonate solution. The slurry was stirred gently while 0.69 g sodium citrate solid was slowly added and then stirred for 2 further hours. After filtering and washing well with distilled water, the solid was calcined in flowing air for 5 hours at 250°C.

Experiment 13 ~1% Au and 0.1% Pd on Alumina

10 g - 60 mesh γ -alumina was slurried into a solution of 0.2 g gold and 0.02 g palladium tetraamine chloride in 50 mL water and one drop of conc. HCl. The slurry was stirred gently as the pH was adjusted to 9.6 with 0.1M sodium carbonate solution. The slurry was again stirred gently while 0.69 g sodium citrate solid was slowly added and then stirred for 2 further hours. After filtering and washing well with distilled water, the solid was calcined in flowing air for 5 hours at 250°C.

EXAMPLES

10 Examples 1-22 were run in batch reactor mode, in stirred 3.5 mL glass vials, sealed with septa and plastic caps. Vials were inserted into a block aluminum heater/stirrer apparatus that holds up to 8 vials. Stirring was done using Teflon®-coated stir bars. Each vial was first charged with 1.5 mL of *n*-octane or undecane solvent, approximately 0.005 or 0.01 g of a given crushed catalyst, a stir
15 bar and the vial was sealed. Vials were stirred and heated approximately 10 minutes to assure that the desired reaction temperature of 125°C had been attained. Next, at the start of each example, 30 μ L of a stock solution of CHHP and TCB(1,2,4-trichlorobenzene) or CB (chlorobenzene), GC (gas chromatograph) internal standard, were injected. Stock solutions consisted of
20 mixtures of about 20 wt % TCB or CB in CHHP. The CHHP source contained up to 2.0 wt % of combined cyclohexanol and cyclohexanone. Vials were removed from the aluminum heater/stirrer after a 0.5 to 10 minute period and were allowed to cool to ambient temperature.

In Examples 1-10 (Table I) vials were analyzed directly for the amount of
25 CHHP remaining, using a 15 m DB-17 capillary column with a 0.32 mm internal diameter. The liquid phase of the column was comprised of (50 wt% phenyl) methyl polysiloxane. The column was obtained from J. and W. Scientific, Folsom, California.

GC analyses for the amounts of CHHP in each solution were calculated
30 using the equation:

$$\text{wt. \% CHHP} = (\text{area \% CHHP/area \% TCB}) \times \text{wt. \% TCB} \times \text{R.F.}_{\text{CHHP}}$$

R.F._{CHHP} (GC response factor for CHHP) was determined from calibration solutions containing known amounts of CHHP and TCB, and was calculated from the equation:

35

$$\text{R.F.}_{\text{CHHP}} = \frac{\text{wt. \% CHHP/area \% CHHP}}{\text{wt. \% TCB/area \% TCB}}$$

$$\% \text{ CHHP Decomp.} = 100 \times [1 - (\text{area } \% \text{ CHHP} / \text{area } \% \text{ TCB})_{\text{final}} / (\text{area } \% \text{ CHHP} / \text{area } \% \text{ TCB})_{\text{initial}}]$$

In Examples 1-10 (Table I) the initial concentrations of CHHP in each vial
5 were approximately 2.2 wt %. The GC wt % CHHP_{initial} and CHHP_{final} numbers
are only approximate because the amount of TCB per g solution ratios used in GC
calculations were arbitrarily all made equal to 0.25 mg TCB/ g solution. Since an
unheated sample of 1.5 mL *n*-octane and 30 μ L CHHP/TCB solution was
analyzed with each set of CHHP decomposition product vials made from the same
10 CHHP/TCB solution, accurate changes in CHHP/TCB ratios could be calculated.

Examples 11-13 (Table II), and Examples 14-16 (Table III), give batch %
t-butylhydroperoxide (t-BuOOH) and % cumenehydroperoxide (CumeneOOH)
decomposition results, respectively for 1% Au/Carbon and 10% Au/SiO₂
catalysts. Analyses for t-BuOOH and CumeneOOH were done using a well
15 known iodometric titration procedure, described in *Comprehensive Analytical
Chemistry*, Elsevier Publishing Company, New York, Eds. C. L. Wilson, p. 756,
1960. Starting and product solutions of t-BuOOH and CumeneOOH in *n*-octane,
followed by adding excess KI/ acetic acid solution, were stirred in sealed vials at
ambient temperature for 10 minutes and were titrated with 0.1 M Na₂S₂O₃
20 solution for amounts of I₂ liberated by the t-BuOOH and CumeneOOH present.

Examples 17-22 (Tables IV&V) were run as described for Examples 1-10
except that the reaction was run at 150°C and chlorobenzene was used as a GC
internal standard in place of TCB and undecane was used in place of *n*-octane
solvent. In Tables IV and V, the amount of initial CHHP and final CHHP in the
25 reaction was determined by calculating the area of the CHHP GC peak divided
by the area of the chlorobenzene GC peak (area % CHHP/area % CB).

TABLE I

EX.	Catalyst	Method of Prep	Approx. Wt% CHHP	Reaction Temp., °C	Time, min.	Wt% CHHP initial	Wt% CHHP final	% CHHP Decomp.
1	1.4% Au/Carbon, 0.0100	Exp. 1	2.2	125	10	0.407	0.221	45.7
2	1.4% Au/Carbon, 0.0103	Exp. 1	2.2	125	10	0.537	0.281	47.7
3	1.4% Au/SiO ₂ , 0.0101	Exp. 2	2.2	125	10	0.407	0.391	3.9
4	1.4% Au/SiO ₂ , 0.0101	Exp. 2	2.2	125	10	0.537	0.430	19.9
5	14% Au/SiO ₂ , 0.0102	Exp. 3	2.2	125	10	0.407	0.154	62.2
6	14% Au/SiO ₂ , 0.0104	Exp. 3	2.2	125	10	0.407	0.131	67.8
7	0% Au/SiO ₂ , 0.0103	Exp. 4	2.2	125	10	0.407	0.379	6.9
8	1.4% Au/Al ₂ O ₃ , 0.0102	Exp. 5	2.2	125	10	0.537	0.449	16.4
9	13% Ag/SiO ₂ , 0.0102	Exp. 6	2.2	125	10	0.407	0.245	39.8
10	4.5% Cu/SiO ₂ , 0.0103	Exp. 7	2.2	125	10	0.407	0.119	70.8

TABLE II

EX.	Catalyst, g	Method of prep.	Reaction Temp., °C	Time, min.	Wt% t-BuOOH initial	Wt% t-BuOOH final	% t-BuOOH Decomp.
11	1.4% Au/Carbon, 0.0102	Exp. 1	125	10	0.35	0.20	44
12	14% Au/SiO ₂ , 0.0102	Exp. 3	125	10	0.35	0.18	48
13	none		125	10	0.35	0.33	5

TABLE III

EX.	Catalyst, g	Method of prep.	Reaction Temp., °C	Time, min.	Wt% t-Cumene-(OOH) initial	Wt% t-Cumene-(OOH) final	% t-Cumene-(OOH) Decomp.
14	1.4% Au/Carbon, 0.0103	Exp. 1	125	10	0.55	0.32	42
15	14% Au/SiO ₂ , 0.0103	Exp. 3	125	10	0.55	0.30	45
16	none		125	10	0.55	0.54	2

TABLE IV

EX.	Catalyst	Method of Prep	Approx. Wt% CHHP	Reaction Temp., °C	Time, min.	CHHP/ CB initial	CHHP/ CB final	% CHHP Decomp.
17	1%Au/MgO, 0.0102	Exp. 8	2.2	150	5	3.41	3.29	3.5
18	1%Au/ γ -Al ₂ O ₃ , 0.0120	Exp. 9	2.2	150	5	3.41	0	100
19	1%Au/SiO ₂ , 0.0101	Exp. 10	2.2	150	5	3.41	0.91	73.3
20	1%Au/TiO ₂ , 0.0106	Exp. 11	2.2	150	5	3.41	2.26	33.6
21	1% Au/ZrO ₂ , 0.0054	Exp. 12	2	150	0.5	5.26	4.68	11.1
22	1% Au, 0.1% Pd/Al ₂ O ₃ , 0.0051	Exp. 13	2	150	0.5	4.82	3.01	37.5

- Examples 23-39 were run in a liquid full plug flow reactor, 30 inches (76 cm) with a ¼ inch (0.64 cm) diameter. Inlet and exit pressure was 150 psig (1.03 MPa gauge) controlled with a back pressure regulator. The catalysts were all prepared as in Experiment 13 on 2 mm spheres with the appropriate metal salts and type of alumina, with the exception that reduction was performed by flowing H₂ at 150°C instead of sodium citrate. The feed consisted of 1.6% CHHP in cyclohexane, about 1% K and 2% A, and varying amounts of water and acid impurities consisting of monobasic and dibasic acids which would be typical of those produced in cyclohexane oxidation such as adipic acid, succinic acid, formic acid, and hydroxycaproic acid, in approximately equal amounts. Analyses were performed on CHHP, K, and A by gas chromatography. Cyclohexane, CHHP, K, and A were obtained from E. I. du Pont de Nemours and Company, Wilmington, DE. The K/A ratio obtained after conversion of cyclohexylhydroperoxide over the catalyst was calculated using the equation:

$$\frac{(\text{mols K in product}) - (\text{mols K in feed})}{(\text{mols A in product}) - (\text{mols A in feed})}$$

TABLE V

Ex.	Catalyst	%CHHP Conv.	K/A
23	1%Au-0.1%Pd/ γ -Al ₂ O ₃	64	1.1
24	1%Au-0.1%Pt/ γ -Al ₂ O ₃	64	1.1
25	1%Au-0.1%Ru/ γ -Al ₂ O ₃	21	1.01
26	1%Au-0.1%Ni/ γ -Al ₂ O ₃	34	1.00
27	1%Au-0.1%Co/ γ -Al ₂ O ₃	45	1.02
28	1%Au-0.1%Pd/ α -Al ₂ O ₃	67	1.91
29	1%Au-0.1%Pt/ α -Al ₂ O ₃	68	1.84

TABLE VI

Ex.	Catalyst	Gas, sccm	%CHHP Conv.	K/A	Feed Benzene, ppm	Exit Benzene, ppm
30	1%Au-0.1%Pd/ α -Al ₂ O ₃	0	60	1.63	-	-
31	1%Au-0.1%Pd/ α -Al ₂ O ₃	N ₂ , 75	62	1.74	-	-
32	1%Au-0.1%Pd/ α -Al ₂ O ₃	H ₂ , 75	78	0.47	-	-
33	1%Au-0.1%Pd/ α -Al ₂ O ₃	H ₂ , 25	66	0.61	-	-
34	1%Au-0.1%Pd/ α -Al ₂ O ₃	H ₂ , 10	61	0.73	-	-
35	1%Au-0.1%Pd/ γ -Al ₂ O ₃	H ₂ , 75	51	0.31	-	-
36	1%Au-0.1%Pd/ α -Al ₂ O ₃	H ₂ , 75	-	-	5140	4828
37	1%Au-0.1%Pd/ α -Al ₂ O ₃	0	-	-	5140	5140
38	1%Au-0.18%Pt/ α -Al ₂ O ₃	0	51	1.84	-	-
39	1%Au-0.18%Pt/ α -Al ₂ O ₃	H ₂ , 75	73	0.41	-	-

We claim:

1. An improved process for decomposing a hydroperoxide to form a decomposition reaction mixture containing a corresponding alcohol and ketone, the improvement comprising decomposing a hydroperoxide by contacting the hydroperoxide with a catalytic amount of a heterogeneous catalyst comprised of gold, wherein 0 to 18% of one or more additional metals selected from the group consisting of Pt, Ru, Ni, and Co are also present with gold.
2. The process according to Claim 1 wherein the heterogeneous catalyst is supported on a catalyst support member.
3. The process according to Claim 2 wherein the catalyst support member is selected from the group consisting of SiO₂, Al₂O₃, carbon, TiO₂, MgO, and zirconia.
4. The process according to Claim 1 wherein the hydroperoxide is cyclohexylhydroperoxide.
5. The process according to Claim 1 or Claim 2 wherein the decomposition reaction temperature is from 80°C to 170°C, and decomposition reaction pressure is from 69 kPa to 2760 kPa.
6. The process according to Claim 5 wherein the reaction pressure is from 276 kPa to 1380 kPa.
7. The process according to Claim 1 or Claim 2 wherein the reaction mixture contains from 0.5 to 100 percent by weight cyclohexyl hydroperoxide.
8. The process according to Claim 1 or Claim 2 wherein the process is run in the presence of cyclohexane.
9. The process according to Claim 1 or Claim 2 wherein the process is run in the presence of added oxygen.
10. The process according to Claim 3 wherein the gold is supported on Al₂O₃.
11. The process according to Claim 10 wherein the gold is from 0.1 to 10 wt. percent of the catalyst and support member.
12. The process according to Claim 2 wherein the gold is present on the support member as well-dispersed particles having a diameter from 3 nm to 15 nm.
13. The process according to Claim 1 wherein the process is run in the presence of hydrogen.