

TITLE
PROCESS FOR THE SELECTIVE
OXIDATION OF ORGANIC COMPOUNDS
FIELD OF THE INVENTION

5 The invention generally relates to a process for oxidizing organic compounds. In particular, the invention relates to a process utilizing hydrogen peroxide to oxidize an oxidizable organic substrate in the presence of a silica-modified titania/silica-containing catalyst and to a preparation of a catalyst using a copolymer of diethoxysilane and ethyl titanate.

10 BACKGROUND OF THE INVENTION

Catalytic oxidation processes are important routes to many commercial chemicals. For example, numerous commercial processes for the epoxidation of olefins have been disclosed in the art. One such process involves the reaction of an organic hydroperoxide with an olefin in the presence of catalytic amounts of
15 certain soluble transition metal compounds (e.g., molybdenum, tungsten, or vanadium naphthenates). Some drawbacks to this process include co-production of an alcohol from the hydroperoxide, recovery of the soluble metal catalyst, and the sensitivity of the reaction to water.

Heterogeneous catalysts which overcome some of the aforesaid problems
20 have also been developed. U.S. Patent No. 3,923,843 claims a process for the epoxidation of an olefinically unsaturated compound comprising reacting the compound in the liquid phase with an organic hydroperoxide in the presence of a catalyst comprising an inorganic siliceous compound in chemical combination with an oxide or hydroxide of titanium. The catalyst is treated with an organic
25 silylating agent before use. In the examples shown, the epoxide selectivity is increased from about 3% to about 15% when comparing the untreated catalyst to the silylated form. The activity for both types of catalyst is about the same.

Hydrogen peroxide is often employed as an oxidizing agent for the production of organic chemicals. A wide variety of organic compounds may be
30 oxidized utilizing hydrogen peroxide, for example, olefins can be oxidized to epoxides (oxiranes) using this reagent.

Many titanosilicates have been reported to be useful as oxidation catalysts. For example, the catalytic oxidation of alkanes and alkenes by titanium silicates is disclosed in C. B. Khouw et al., "Studies on the Catalytic Oxidation of Alkanes
35 and Alkenes by Titanium Silicates", Journal of Catalysis 149, 195-205 (1994). Such catalysts are used for the selective oxidation of n-octane using organic hydroperoxides as the oxidants at temperatures below 100°C. The absence of water is deemed critical for catalytic activity.

(e) aliphatic hydrocarbons of the formula C_qH_{2q+2} , wherein q is an integer from 1 to 20; and

(f) alcohols according to the formula $R^{10}R^{11}CHOH$, wherein R^{10} and R^{11} are each independently -H; alkyl, wherein the alkyl group has from 1 to 16 carbon atoms; alkylaryl, wherein the alkylaryl group has from 7 to 16 carbon atoms; cycloalkyl, wherein the cycloalkyl group has from 6 to 10 carbon atoms; cycloalkyl wherein R^{10} and R^{11} taken together form a link containing 4 to 11 $-CH_2-$ groups; or alkylcycloalkyl, wherein the alkylcycloalkyl group has from 7 to 16 carbon atoms.

10 The invention also provides a process for the preparation of a molecular sieve catalyst comprising synthesizing a catalyst comprising oxides of silicon and titanium by contacting the catalyst with a copolymer of diethoxysilane and ethyl titanate to form a molecular sieve catalyst.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

15 Hydrogen peroxide-activating metals include, for example, silver, cobalt, cerium, manganese, iron, copper, molybdenum, tungsten, vanadium, titanium, chromium and mixtures thereof. Metallosilicates containing the above metals can be prepared in a similar manner to that described in R. Neumann et al., "Metal Oxide (TiO_2 , MoO_3 , WO_3) Substituted Silicate Xerogels as Catalysts for the
20 Oxidation of Hydrocarbons with Hydrogen Peroxide", Journal of Catalysis, 166, pp. 206-217 (1997).

A presently preferred metal is tetrahedrally coordinated titanium. Metallosilicates which can contain tetrahedrally coordinated titanium include the following molecular sieve structures: silicalite-1 (TS-1), silicalite-2 (TS-2),
25 zeolite-beta, silicon analogs of ZSM-48 and MCM-41. (See R. Murugavel and H. W. Roesky, "Titanosilicates: Recent Developments in Synthesis and Use as Oxidation Catalysts", Angew. Chem. Int. Ed. Engl., 36, No. 5, pp. 477-479 (1997) for a discussion of titanosilicates, their synthesis, and use as oxidation catalysts).

In one embodiment, crystalline titanium silicalite is used as the catalyst.
30 The preparation of porous crystalline titanium silicalite (TS-1) which corresponds to the formula, $xTiO_2(1-x)SiO_2$, where x is between about 0.0005 and about 0.04 has been disclosed in U.S. Patent No. 4,410,501 the contents of which are incorporated herein by reference. TS-1 has been shown to catalyze numerous reactions including the following selective oxidations; aromatic hydroxylations,
35 alkane oxidations and alkene epoxidations. The oxidation reactions are performed using dilute (40% or less) aqueous hydrogen peroxide. The reactions are typically run at 100°C or less and at atmospheric pressure.

Some examples of molecular sieve catalysts prepared by the process of this invention include materials having MFI, MEL, M41S, MOR and BEA type

vapor. The silylation may be carried out as a batch, semi-continuous or continuous process.

The time required for the silylating agent to react with the catalyst surface is dependent on the temperature and agent used. Lower temperatures require longer reaction times. Typically, times of from about 0.1 to about 48 hours are suitable.

Although there is no limit to the amount of silylating agent used, for practical reasons it is believed that it can vary from about 1% to about 1000% by weight of the entire catalyst composition. The silylating agent can be applied to the catalyst either in one or a series of treatments.

A wide variety of organic compounds can be oxidized by the process of this invention. Presently preferred organic compounds are listed above in the "Summary of the Invention".

Olefins useful in the process of this invention may be any organic compound having at least one ethylenically unsaturated functional group (i.e., a carbon-carbon double bond) and may be a cyclic, branched, or straight chain olefin. The olefin is reacted with hydrogen peroxide to produce an epoxide (oxirane). The olefin may contain aryl groups such as phenyl. Preferably, the olefin is an aliphatic compound containing from 2 to 20 carbon atoms. Multiple double bonds may be present in the olefin, e.g., dienes, trienes, and other polyunsaturated substrates. The double bond may be in a terminal or internal position of the olefin or may form part of a cyclic structure as in cyclohexene. Other, non-limiting examples of suitable organic compounds include unsaturated fatty acids or esters and oligomeric or polymeric unsaturated compounds such as polybutadiene.

The olefin may optionally contain functional groups such as halide, carboxylic acid, ether, hydroxy, thio, nitro, cyano, ketone, acyl, ester, amino, and anhydride.

Preferred olefins include ethylene, propylene, butenes, butadiene, pentenes, isoprene, and hexenes.

Mixtures of olefins may be epoxidized and the resulting mixtures of epoxides may be used in mixed form or separated into the component epoxides.

Olefins especially preferred for the process of this invention include those of the formula $R^1R^2C=CR^3R^4$, wherein R^1 , R^2 , R^3 and R^4 are each independently selected from the group consisting of H and C_1 to C_{12} straight chain, saturated, or unsaturated hydrocarbon radicals.

Cyclic ketones useful in the process of this invention include cyclopentanone, cyclohexanone. The cyclic ketone is reacted with the in-situ generated hydrogen peroxide to produce lactones. For example, cyclopentanone

The oxidation products are recovered from the product mixtures by conventional techniques such as fractional distillation, extraction, and crystallization.

- Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following specific embodiments are, therefore, to be construed as merely illustrative, and are not to limit the remainder of the invention in any way whatsoever. All percentages are by weight unless otherwise indicated.

EXAMPLES

10 Preparation of Catalyst A

Titanium isopropoxide (28.4 g) and isopropyl alcohol (IPA, 30 mL) were mixed and acetylacetone (10.01 g) in IPA (10 mL) was added. The resulting solution was heated to reflux for one hour and then cooled. The IPA was removed under vacuum and the resultant solid was redissolved in IPA to make up 100 mL.

- 15 The solution was 1 molar in Ti.

- A portion of the above solution (25.0 mL) was mixed with tetramethylorthosilicate (TMOS, 45.66 mL) and IPA (44 mL). To this was added, dropwise with stirring, a solution of conc. HCl (2.4 mL), H₂O (29.2 g) and IPA (30 mL). This mixture was stirred for 5 min. at room temperature and additional
20 IPA (168 mL) was added. The gel mixture was aged for 64 hours at room temperature with stirring, and thickened slightly.

The sol-gel was extracted with supercritical CO₂ at 40°C at 3500 psig (24.2 MPa) for 5 hours. The resulting fluffy yellow powder was calcined as follows: 400°C for 1 hour in N₂ followed by 600°C for 5 hours in air.

- 25 Catalyst A was x-ray amorphous.

Preparation of Catalyst A2

The procedure for the preparation of Catalyst A was followed except that the gel mixture was aged for 90 hours.

Preparation of Catalyst B

- 30 To Catalyst A (0.508 g) was added a mixture of N,O-bis(trimethylsilyl)-trifluoroacetamide (i.e., CF₃C(OSi(CH₃)₃)=NSi(CH₃)₃ or BSTFA; 1.0 g) and toluene (7.96 g). The mixture was stirred for two hours at room temperature, filtered, the solids washed with toluene, and air dried.

Preparation of Catalyst B2

- 35 To Catalyst A (1.02 g) was added a mixture of 1.05 g BSTFA (1.05 g) and toluene (7.87 g). The slurry mixture was stirred for two hours at room temperature, filtered, the solids washed with toluene, and air dried.

EXAMPLE 1**Epoxidation of 1-Octene**

To Catalyst B (50 mg) was added 3% aqueous hydrogen peroxide (1.09 g) and 1-octene (2.05 g). The mixture was stirred at room temperature. After 24 hrs, GC analysis showed the presence of 1,2-epoxyoctane in 90% selectivity (18% yield based on peroxide).

EXAMPLE 2**Epoxidation of 1-Octene**

To Catalyst B2 (98 mg) was added 3% aqueous hydrogen peroxide (1.03 g) and 1-octene (2.14 g). The mixture was stirred at room temperature. After 24 hrs, GC analysis showed the presence of 1,2-epoxyoctane in 90% selectivity (11% yield based on peroxide).

EXAMPLE 3**Epoxidation of cis-Cyclooctene**

To Catalyst B2 (91 mg) was added 10% aqueous hydrogen peroxide (1.05 g) and cis-cyclooctene (2.44 g). The mixture was stirred at room temperature. After 24 hours, GC analysis showed the presence of cyclooctene oxide in 33% yield based on peroxide.

COMPARATIVE EXAMPLE A**Epoxidation of 1-Octene**

To Catalyst A (41 mg) was added 3% aqueous hydrogen peroxide (1.02 g) and 1-octene (2.02 g). The mixture was stirred at room temperature. After 24 hrs, GC analysis showed the presence of a trace of 1,2-epoxyoctane (<0.2% yield based on peroxide).

COMPARATIVE EXAMPLE B**Epoxidation of 1-Octene**

To Catalyst A2 (118 mg) was added 3% aqueous hydrogen peroxide (1.04 g) and 1-octene (2.11 g). The mixture was stirred at room temperature. After 24 hrs, GC analysis showed the presence of a trace of 1,2-epoxyoctane (<0.6% yield based on peroxide).

COMPARATIVE EXAMPLE C**Epoxidation of cis-Cyclooctene**

To Catalyst A2 (100 mg) was added 10% aqueous hydrogen peroxide (1.01 g) and cis-cyclooctene (2.43 g). The mixture was stirred at room temperature. After 24 hours, GC analysis showed no reaction to cyclooctene oxide.

COMPARATIVE EXAMPLE F

Epoxidation of 1-Octene

To 0.101 g of titanasilicalite prepared as Catalyst G above (before silylation) was added 1-octene (2.06 g) and 1.05 g of 10 wt % aqueous H_2O_2 .

- 5 After stirring at room temperature for 24 hours, GC analysis showed the presence of 1,2-epoxyoctane in 90% selectivity (6% yield based on peroxide).

COMPARATIVE EXAMPLE G

Epoxidation of cis-Cyclooctene

- 10 To Catalyst G before silylation (55 mg) was added 10% aqueous hydrogen peroxide (1.08 g) and cis-cyclooctene (2.63 g). The mixture was stirred at room temperature. After 24 hours, GC analysis showed no reaction to cyclooctene oxide.

EXAMPLE 8

- 15 The titanium precursor used in Examples 8 to 10 was Gelest diethoxy-siloxane-ethyltitanate copolymer (# in Gelest catalogue = PSITI-019), $[(\text{C}_2\text{H}_5\text{O})_2\text{SiO}][(\text{C}_2\text{H}_5\text{O})_2\text{TiO}]$, 19.1-19.6% Si, 2.1-2.3% Ti. Atomic ratio Si:Ti about 15.

Alkaline Synthesis of Mesoporous $\text{SiO}_2/\text{TiO}_2$

- 20 Cetyltrimethylammoniumbromide (6.44 g) was dissolved in tetramethylammoniumhydroxide (26.98 g). The PSITI-019 precursor (20.0 g) was added dropwise with strong agitation. The mixture was stirred at 25°C for 3 days and 17 hours. The products were filtered and washed with distilled H_2O (1 L). The dried white solids were calcined by heating in air at 1°C/min to 550°C, which was maintained for 4 hours before cooling.

- 25 Long range mesoporous order was demonstrated by an XRD peak at 3.2 nm. UV/Visible spectroscopy showed that isolated, as well as oligomeric Ti was present. A very intense band at 960 cm^{-1} in the infrared lends further evidence for framework Ti. The high Ti content in the sample (Si:Ti = 8) was probably the reason for the oligomeric Ti species.

EXAMPLE 9

Acidic Synthesis of Mesoporous $\text{SiO}_2/\text{TiO}_2$

- 35 Cetyltrimethylammoniumbromide (3.22 g) was dissolved in dilute HCl made by combining 36.6 g conc. HCl and 148.5 g H_2O . The PSITI-019 precursor (10.0 g) was added dropwise with strong agitation. The mixture was stirred at 25°C for 3 days and 17 hours. The products were filtered and washed with distilled H_2O (1 L). The dried white solids were calcined by heating in air at 1°C/min to 550°C, which was maintained for 4 hours before cooling.

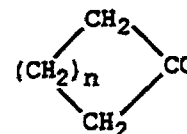
CLAIMS:

1. A process for oxidizing organic compounds comprising:
 contacting, in a zone of reaction, an oxidizable organic compound
 with hydrogen peroxide in the presence of a catalytically effective amount of an
 5 insoluble catalyst comprising silicon oxide and an oxide of at least one hydrogen
 peroxide-activating metal, which catalyst has been treated with a silylating agent,
 and wherein the activity of the treated catalyst is increased by a factor of at least
 two compared to untreated catalyst.

2. The process of Claim 1 wherein the organic compound is selected
 10 from the group consisting of:

(a) cyclic olefins and olefins according to the formula
 $R^1R^2C=CR^3R^4$,

- wherein R^1 , R^2 , R^3 and R^4 are each independently -H;
 alkyl, wherein the alkyl group has from 1 to 16 carbon atoms; alkylaryl, wherein
 15 the alkylaryl group has from 7 to 16 carbon atoms; cycloalkyl, wherein the
 cycloalkyl group has from 6 to 10 carbon atoms; or alkylcycloalkyl, wherein the
 alkylcycloalkyl group has from 7 to 16 carbon atoms; and wherein said olefin can
 optionally containing halogen atoms (i.e., Cl, Br, F, and I);



(b) cyclic ketones according to the formula

- 20 wherein n is an integer from 2 to 9;

(c) compounds of the formula $C_6H_5R^5$, wherein R^5 is -H, -OH; C_1
 to C_3 straight chain, saturated or unsaturated hydrocarbon radicals, $-CO_2H$; $-CN$;
 $-COC_m$, wherein m is an integer from 1 to 6; $-OC_m$, wherein m is an integer from
 1 to 6; or NR^6R^7 , where R^6 and R^7 are each independently -H or C_1 to C_3 alkyl
 25 groups;

(d) alicyclic hydrocarbons according to the formula $R^8R^9CH_2$,

wherein R^8 and R^9 together form a link of $(-CH_2-)_p$,
 wherein p is an integer from 4 to 11;

- (e) aliphatic hydrocarbons of the formula C_qH_{2q+2} , wherein q is an
 30 integer from 1 to 20; and

(f) alcohols according to the formula $R^{10}R^{11}CHOH$, wherein R^{10}
 and R^{11} are each independently -H; alkyl, wherein the alkyl group has from 1 to
 16 carbon atoms; alkylaryl, wherein the alkylaryl group has from 7 to 16 carbon
 atoms; cycloalkyl, wherein the cycloalkyl group has from 6 to 10 carbon atoms;
 35 cycloalkyl wherein R^{10} and R^{11} taken together form a link containing 4 to