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(54) Title: EPOXIDATION CATALYST

(57) Abstract: Titanium or vanadium zeolite catalysts are prepared by reacting a titanium or vanadium compound, a silicon source, a templating agent, and a hydrophobic hydrocarbon liquid polymer. The catalyst is useful in olefin epoxidation with hydrogen peroxide.



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EPOXIDATION CATALYST

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FIELD OF THE INVENTION

This invention relates to a process for producing a titanium or vanadium zeolite catalyst and its use in olefin epoxidation with hydrogen peroxide.

BACKGROUND OF THE INVENTION

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Many different methods for the preparation of epoxides have been developed. Generally, epoxides are formed by the reaction of an olefin with an oxidizing agent in the presence of a catalyst. The production of propylene oxide from propylene and an organic hydroperoxide oxidizing agent, such as ethyl benzene hydroperoxide or tert-butyl hydroperoxide, is commercially practiced technology, see, e.g., U.S. Pat. Nos. 3,351,635 and 4,367,342. Another commercially practiced technology is the direct epoxidation of ethylene to ethylene oxide by reaction with oxygen over a silver catalyst. Unfortunately, the silver catalyst has not proved useful in commercial epoxidation of higher olefins.

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Besides oxygen and organic hydroperoxides, another oxidizing agent useful for the preparation of epoxides is hydrogen peroxide. U.S. Pat. No. 4,833,260, for example, discloses the epoxidation of olefins with hydrogen peroxide in the presence of a titanium silicalite catalyst. Much current research is conducted in the direct epoxidation of olefins with oxygen and hydrogen. Many different direct epoxidation catalysts have been proposed. Typically, the catalyst comprises a noble metal that is supported on a titanosilicate. For example, JP 4-352771 discloses the formation of propylene oxide from propylene, oxygen, and hydrogen using a catalyst containing a Group VIII metal such as palladium on a titanium silicalite. Other direct epoxidation catalyst examples include gold supported on titanosilicates, see, e.g., PCT Intl. Appl. WO 98/00413.

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Titanium and vanadium silicalites are typically produced by a hydrothermal crystallization procedure, for example, as described in U.S. Pat. Nos. 4,410,501 and 4,833,260. Typical catalyst syntheses produce small crystals of less than 1 micron. Unfortunately, the small particle size is problematic in commercial epoxidation of alkenes. In fixed bed processes, the

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small particle size creates an enormous pressure drop which renders the process unworkable, while in slurry processes, separation of the catalyst from the liquid reactor contents is extremely difficult or results in plugging process filters.

5 To improve the longevity of the olefin epoxidation process, small titanium silicalite crystals have been conglomerated into formed particles of larger size through the use of binders, as taught, for example, by U.S. Pat. Nos. 5,500,199 and 6,106,803. However, the use of binders obscure portions of the zeolite structure, thus effectively removing catalytic sites in the reaction. The formed
10 particles are also subject to attrition as the conglomerates break apart. One method to overcome these disadvantages is the production of large crystal size titanium silicalite, see for example U.S. Pat. No. 6,960,671.

 U.S. Pat. No. 7,288,237, U.S. Appl. Pub. No. 2007/0112209, and
15 copending Application Ser. No. 12/072,575 disclose the preparation of titanium or vanadium zeolite catalysts by reacting a titanium or vanadium compound, a silicon source, and a templating agent, in the presence of a hydrocarbon and a surfactant (U.S. Pat. No. 7,288,237), or a polyol (U.S. Appl. Pub. No. 2007/0112209), or a hydrophobic hydrocarbon wax (Application Ser. No. 12/072,575). However, none of these procedures result in large particle size
20 zeolites.

 As with any chemical process, it is desirable to attain still further improvements in the epoxidation methods and catalysts. We have discovered an effective, convenient process to form a large particle epoxidation catalyst and its use in the epoxidation of olefins.

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SUMMARY OF THE INVENTION

 The invention is a process for producing a titanium or vanadium zeolite catalyst. The process comprises reacting a titanium or vanadium compound, a silicon source, a templating agent, and a hydrophobic hydrocarbon liquid
30 polymer at a temperature and for a time sufficient to form a molecular sieve. The process is effective at producing large zeolite particles that are useful in the epoxidation of olefins with hydrogen peroxide.

DETAILED DESCRIPTION OF THE INVENTION

The process of the invention is used to produce titanium or vanadium zeolites. Titanium or vanadium zeolites comprise the class of zeolitic substances wherein titanium or vanadium atoms are substituted for a portion of the silicon atoms in the lattice framework of a molecular sieve. Such substances, and their production, are well known in the art. See for example, U.S. Pat. Nos. 4,410,501 and 4,833,260.

The process of the invention comprises reacting a titanium or vanadium compound, a silicon source, a templating agent, and a liquid polymer at a temperature and for a time sufficient to form a molecular sieve. In a preferred embodiment of the invention, the titanium or vanadium compound, silicon source, templating agent, and liquid polymer are reacted in the presence of a surfactant and an optional additional hydrocarbon. The process is typically performed in the presence of water. Other solvents such as alcohols may also be present. Alcohols such as isopropyl, ethyl and methyl alcohol are preferred, and isopropyl alcohol is especially preferred.

Although the process of the invention is not limited by choice of a particular titanium or vanadium compound, suitable titanium or vanadium compounds useful in the invention include, but are not limited to, titanium or vanadium alkoxides, titanium or vanadium halides, and mixtures thereof. Preferred titanium alkoxides are titanium tetraisopropoxide, titanium tetraethoxide and titanium tetrabutoxide. Titanium tetraethoxide is especially preferred. Preferred titanium halides include titanium trichloride and titanium tetrachloride.

Suitable silicon sources include, but are not limited to, colloidal silica, fumed silica, silicon alkoxides, and mixtures thereof. Preferred silicon alkoxides are tetraethylorthosilicate, tetramethylorthosilicate, and the like. Tetraethylorthosilicate is especially preferred.

The templating agent is typically a tetraalkylammonium hydroxide, tetraalkylammonium halide, tetraalkylammonium nitrate, tetraalkylammonium acetate, and the like, and mixtures of templating agents. Tetraalkylammonium hydroxides and tetraalkylammonium halides, such as tetrapropylammonium hydroxide and tetrapropylammonium bromide, are preferred. Tetrapropylammonium hydroxide is especially preferred.

The hydrophobic hydrocarbon liquid polymer is a hydrocarbon polymer that is liquid at temperatures in the range of from about 25°C to about 40°C. The number average molecular weight of the hydrophobic hydrocarbon liquid polymer is preferably between about 500 and 5,000. Hydrophobic hydrocarbon liquid polymers most suitable for use in the preparation of the titanium or vanadium zeolite include liquid polyisobutylene, liquid polybutadiene, liquid polyisoprene, and mixtures thereof. The liquid polyisobutylene, liquid polybutadiene, and liquid polyisoprene may be homopolymers or may incorporate minor amounts of other monomers. Low-molecular-weight liquid polyisobutylenes and liquid polybutadienes are particularly preferred. Low-molecular-weight liquid polyisobutylenes are most preferred.

The optional surfactant may be any suitable nonionic, ionic, cationic or amphoteric surfactant. Preferably, the surfactant is a nonionic surfactant, such as alkoxylated adducts of alcohols, diols, or polyols. Such surfactants typically comprise the condensation product of one mole of alcohol (or diol or polyol) with 1 to about 50, preferably 1 to about 20, more preferably 2 to about 10, moles of ethylene oxide (EO) or propylene oxide (PO). Suitable surfactants include the alkylene oxide adducts of acetylenic diols such as the Surfynol® products from Air Products, which comprise the ethoxylated adducts of 2,4,7,9-tetramethyl-5-decyne-4,7-diol. Suitable surfactants also include polyoxyethylene polyoxypropylene alkyl ether, polyoxyethylene alkyl ether, polyoxyethylene alkylallyl ether, polyoxyethylene alkylaryl ether, polyoxyethylene nonylphenyl ether such as Igepal® CO-720 available from Aldrich, polyoxyethylene octylphenyl ether, and mixtures thereof. Of these, polyoxyethylene alkyl ethers and polyoxyethylene alkylaryl ethers are most preferred. Particularly preferred are polyoxethylene nonylphenyl ether, polyoxethylene octylphenyl ether, and the like.

The optional hydrocarbon preferably does not contain any oxygen atoms. Preferred hydrocarbons include C₅-C₁₂ aliphatic hydrocarbons (straight chain, branched, or cyclic), C₆-C₁₂ aromatic hydrocarbons (including alkyl-substituted aromatic hydrocarbons), C₁-C₁₀ halogenated aliphatic hydrocarbons, C₆-C₁₂ halogenated aromatic hydrocarbons, and mixtures thereof. Examples of suitable hydrocarbons include n-hexane, n-heptane, cyclopentane, methyl pentanes, cyclohexane, methyl cyclohexane, dimethyl hexanes, toluene, xylenes,

methylene chloride, chloroform, dichloroethanes, chlorobenzene, benzyl chloride, and the like.

Preferred hydrocarbons also include hydrophobic hydrocarbon waxes. Hydrophobic hydrocarbon wax is typically a long-chain hydrocarbon having a melting point greater than 40°C, preferably from 45°C to 175°C. Hydrophobic hydrocarbon waxes most suitable for use in the preparation of the titanium or vanadium zeolite include polyolefin waxes (such as low-molecular-weight polyethylene wax, polypropylene wax, and polyisobutylene wax), microcrystalline waxes, Fischer-Tropsch waxes, paraffin waxes, and mixtures thereof. Low-molecular-weight polyethylene waxes are particularly preferred. The number average molecular weight of the low-molecular-weight polyethylene wax is preferably between about 400 and 5,000. Commercially available hydrophobic hydrocarbon waxes include POLYWAX® polyethylene waxes, VYBAR® polyolefin waxes, and BARECO® microcrystalline waxes (available from Baker Petrolite Co.) and Sasolwax® paraffin and Fischer-Tropsch waxes (available from Sasol Wax Co.).

Generally, the hydrothermal process used to prepare titanium or vanadium zeolites involves forming a reaction mixture wherein the molar ratios of additives (as defined in terms of moles of templating agent, moles of SiO₂ and moles of TiO₂ or VO_{2.5}) preferably comprise the following molar ratios: TiO₂(VO_{2.5}):SiO₂ = 0.5-5:100; and templating agent:SiO₂ = 10-50:100. The water:SiO₂ molar ratio is preferably from about 1000-5000:100 and the solvent:SiO₂ molar ratio may be in the range of 0-500:100. The titanium or vanadium source, silicon source, templating agent, and water (and solvent, if added) combined together form a clear gel mother liqueur. The weight ratio of liquid polymer:clear gel is preferably from about 0.005 to about 2. If used, the weight ratio of surfactant:clear gel is preferably from about 0.01 to about 0.25.

The reaction mixture may be prepared by mixing the desired sources of titanium or vanadium, silicon, and templating agent with the liquid polymer and optional surfactant and optional hydrocarbon to form a reaction mixture. After forming the reaction mixture, it is also typically necessary that the mixture have a pH of about 9 to about 13. The basicity of the mixture is controlled by the amount of templating agent (if it is in the hydroxide form) which is added and/or the use of other basic compounds. If another basic compound is used, the basic

compound is preferably an organic base that is free of alkali metals, alkaline earth metals, and the like. The addition of other basic compounds may be needed if the templating agent is added as a salt, e.g., halide or nitrate. Examples of these basic compounds include ammonium hydroxide, quaternary ammonium hydroxides and amines. Specific examples include tetraethylammonium hydroxide, tetrabutylammonium hydroxide, n-butylamine, and tripropylamine.

The order of addition of the titanium or vanadium compound, silicon source, templating agent, liquid polymer and optional surfactant and optional hydrocarbon to form the reaction mixture is not considered critical to the invention. For instance, these compounds can be added all at once to form the reaction mixture. Alternatively, the reaction mixture may be prepared by first mixing the desired sources of titanium or vanadium, silicon, and templating agent to give an initial reaction mixture. If necessary, the initial reaction mixture may be adjusted to a pH of about 9 to about 13 as described above. Hydrophobic hydrocarbon liquid polymer (and optional surfactant and optional hydrocarbon) is then added to the initial reaction mixture to form the reaction mixture.

After the reaction mixture is formed, it is reacted at a temperature and a time sufficient to form a molecular sieve. Preferably, the reaction mixture is heated at a temperature of about 100°C to about 250°C for a period greater than about 0.25 hours (preferably less than about 96 hours). Preferably, the reaction mixture is heated in a sealed vessel under autogenous pressure. Preferably, the reaction mixture is heated at a temperature range from about 125°C to about 200°C, most preferably from about 150°C to about 180°C. After the desired reaction time, the titanium or vanadium zeolite is recovered. Suitable zeolite recovery methods include filtration and washing (typically with deionized water), rotary evaporation, centrifugation, and the like. The titanium or vanadium zeolite may be dried at a temperature greater than about 20°C, preferably from about 50°C to about 200°C.

As synthesized, the titanium or vanadium zeolites of this invention will contain some of the templating agent or the additional basic compounds in the pores. Any suitable method to remove the templating agent may be employed. The template removal may be performed by a high temperature heating in the presence of an inert gas or an oxygen-containing gas stream. Alternatively, the

template may be removed by contacting the zeolite with ozone at a temperature of from 20°C to about 800°C. The zeolite may also be contacted with an oxidant such as hydrogen peroxide (or hydrogen and oxygen to form hydrogen peroxide in situ) or peracids to remove the templating agent. The zeolite may also be
5 contacted with an enzyme, or may be exposed to an energy source such as microwaves or light in order to decompose the templating agent.

Preferably, the titanium or vanadium zeolite is heated at temperatures greater than 250°C to remove the templating agent. Temperatures of from about 275°C to about 800°C are preferred, and most preferably from about 300°C to
10 about 600°C. The high temperature heating may be conducted in inert atmosphere which is substantially free of oxygen, such as nitrogen, argon, neon, helium or the like or mixture thereof. By "substantially free of oxygen," it is meant that the inert atmosphere contains less than 10,000 ppm mole oxygen, preferably less than 2000 ppm. Also, the heating may be conducted in an
15 oxygen-containing atmosphere, such as air or a mixture of oxygen and an inert gas. Alternatively, the titanium or vanadium zeolite may also be heated in the presence of an inert gas such as nitrogen prior to heating in an oxygen-containing atmosphere. The heating process may be conducted such that the gas stream (inert, oxygen-containing, or both) is passed over the titanium or
20 vanadium zeolite. Alternatively, the heating may be performed in a static manner. The zeolite could also be agitated or stirred while being contacted with the gas stream.

The titanium or vanadium zeolites produced by the process of the invention typically have a majority of particles having large particle size of
25 greater than about 5 microns (and generally less than about 500 microns) with high productivity in the epoxidation of olefins with hydrogen peroxide. Thus, it is not necessary to form larger particles by standard techniques, although the as-synthesized titanium or vanadium zeolite may optionally be spray dried, pelletized or extruded prior to the heating step. If spray dried, pelletized or
30 extruded, the titanium or vanadium zeolite may additionally comprise a binder or the like and may be molded, spray dried, shaped or extruded into any desired form prior the heating step.

The titanium zeolite preferably is of the class of molecular sieves commonly referred to as titanium silicalites, particularly "TS-1" (having an MFI

topology analogous to that of the ZSM-5 aluminosilicate zeolites), "TS-2" (having an MEL topology analogous to that of the ZSM-11 aluminosilicate zeolites), "TS-3" (as described in Belgian Pat. No. 1,001,038), and Ti-MWW (having an MEL topology analogous to that of the MWW aluminosilicate zeolites). Titanium-containing molecular sieves having framework structures isomorphous to zeolite beta, mordenite, ZSM-48, ZSM-12, SBA-15, TUD, HMS, and MCM-41 can also be produced.

The epoxidation process of the invention comprises contacting an olefin and hydrogen peroxide in the presence of the titanium or vanadium zeolite catalyst. Suitable olefins include any olefin having at least one carbon-carbon double bond, and generally from 2 to 60 carbon atoms. Preferably the olefin is an acyclic alkene of from 2 to 30 carbon atoms; the process of the invention is particularly suitable for epoxidizing C₂-C₆ olefins. More than one double bond may be present, as in a diene or triene for example. The olefin may contain only carbon and hydrogen atoms, or may contain functional groups such as halide, carboxyl, hydroxyl, ether, carbonyl, cyano, or nitro groups, or the like. The process of the invention is especially useful for converting propylene to propylene oxide.

The hydrogen peroxide may be generated prior to use in the epoxidation reaction. Hydrogen peroxide may be derived from any suitable source, including oxidation of secondary alcohols such as isopropanol, the anthraquinone process, and from direct reaction of hydrogen and oxygen. The concentration of the aqueous hydrogen peroxide reactant added into the epoxidation reaction is not critical. Typical pre-formed hydrogen peroxide concentrations range from 0.1 to 90 weight percent hydrogen peroxide in water, preferably 1 to 5 weight percent.

The amount of pre-formed hydrogen peroxide to the amount of olefin is not critical, but most suitably the molar ratio of hydrogen peroxide:olefin is from 100:1 to 1:100, and more preferably in the range of 10:1 to 1:10. One equivalent of hydrogen peroxide is theoretically required to oxidize one equivalent of a mono-unsaturated olefin substrate, but it may be desirable to employ an excess of one reactant to optimize selectivity to the epoxide.

The hydrogen peroxide may also be generated in situ by the reaction of hydrogen and oxygen in the presence of a noble metal catalyst. Although any sources of oxygen and hydrogen are suitable, molecular oxygen and molecular

hydrogen are preferred. Thus, in one preferred embodiment of the invention, the epoxidation of olefin, hydrogen and oxygen is carried out in the presence of a noble metal catalyst and the titanium or vanadium zeolite produced by the methods described above.

5 While any noble metal catalyst can be utilized (i.e., gold, silver, platinum, palladium, iridium, ruthenium, osmium metal catalysts), either alone or in combination, palladium, platinum and gold metal catalysts are particularly desirable. Suitable noble metal catalysts include high surface area noble metals, noble metal alloys, and supported noble metal catalysts. Examples of suitable
10 noble metal catalysts include high surface area palladium and palladium alloys. However, particularly preferred noble metal catalysts are supported noble metal catalysts comprising a noble metal and a support.

For supported noble metal catalysts, the support is preferably a porous material. Supports are well-known in the art. There are no particular restrictions
15 on the type of support that are used. For instance, the support can be inorganic oxides, inorganic chlorides, carbon, and organic polymer resins. Preferred inorganic oxides include oxides of Group 2, 3, 4, 5, 6, 13, or 14 elements. Particularly preferred inorganic oxide supports include silica, alumina, titania, zirconia, niobium oxides, tantalum oxides, molybdenum oxides, tungsten oxides,
20 amorphous titania-silica, amorphous zirconia-silica, amorphous niobia-silica, and the like. Preferred organic polymer resins include polystyrene, styrene-divinylbenzene copolymers, crosslinked polyethyleneimines, and polybenzimidazole. Suitable supports also include organic polymer resins grafted onto inorganic oxide supports, such as polyethylenimine-silica. Preferred
25 supports also include carbon. Particularly preferred supports include carbon, silica, silica-aluminas, titania, zirconia, and niobia.

Preferably, the support has a surface area in the range of about 10 to about 700 m²/g, more preferably from about 50 to about 500 m²/g, and most preferably from about 100 to about 400 m²/g. Preferably, the pore volume of the
30 support is in the range of about 0.1 to about 4.0 mL/g, more preferably from about 0.5 to about 3.5 mL/g, and most preferably from about 0.8 to about 3.0 mL/g. Preferably, the average particle size of the support is in the range of about 0.1 to about 500 μm, more preferably from about 1 to about 200 μm, and most preferably from about 10 to about 100 μm. The average pore diameter is

typically in the range of about 10 to about 1000 Å, preferably about 20 to about 500 Å, and most preferably about 50 to about 350 Å.

The supported noble metal catalyst contains a noble metal. While any of the noble metals can be utilized (i.e., gold, silver, platinum, palladium, iridium, ruthenium, osmium), either alone or in combination, palladium, platinum, gold, and mixtures thereof are particularly desirable. Typically, the amount of noble metal present in the supported catalyst will be in the range of from 0.001 to 20 weight percent, preferably 0.005 to 10 weight percent, and particularly 0.01 to 5 weight percent. The manner in which the noble metal is incorporated into the supported catalyst is not considered to be particularly critical. For example, the noble metal may be supported by impregnation, adsorption, precipitation, or the like. Alternatively, the noble metal can be incorporated by ion-exchange with, for example, tetraammine palladium dichloride.

There are no particular restrictions regarding the choice of noble metal compound or complex used as the source of the noble metal in the supported catalyst. For example, suitable compounds include the nitrates, sulfates, halides (e.g., chlorides, bromides), carboxylates (e.g. acetate), and amine complexes of noble metals.

Depending on the olefin to be reacted, the epoxidation according to the invention can be carried out in the liquid phase, the gas phase, or in the supercritical phase. When a liquid reaction medium is used, the catalyst is preferably in the form of a suspension or fixed-bed. The process may be performed using a continuous flow, semi-batch or batch mode of operation.

If epoxidation is carried out in the liquid (or supercritical) phase, it is advantageous to work at a pressure of 1-200 bars and in the presence of one or more solvents. Suitable solvents include, but are not limited to, alcohols, ketones, water, CO₂, or mixtures thereof. Suitable alcohols include C₁-C₄ alcohols such as methanol, ethanol, isopropanol, and tert-butanol, or mixtures thereof. If CO₂ is used as a solvent, the CO₂ may be in the supercritical state or in a high pressure/subcritical state. Fluorinated alcohols can be used. It is preferable to use mixtures of the cited alcohols with water.

If epoxidation is carried out in the liquid (or supercritical) phase, it is advantageous to use a buffer. The buffer will typically be added to the solvent to form a buffer solution. The buffer solution is employed in the reaction to inhibit

the formation of glycols or glycol ethers during epoxidation. Buffers are well known in the art.

Buffers useful in this invention include any suitable salts of oxyacids, the nature and proportions of which in the mixture, are such that the pH of their solutions may preferably range from 3 to 12, more preferably from 4 to 10 and most preferably from 5 to 9. Suitable salts of oxyacids contain an anion and cation. The anion portion of the salt may include anions such as phosphate, carbonate, bicarbonate, carboxylates (e.g., acetate, phthalate, and the like), citrate, borate, hydroxide, silicate, aluminosilicate, or the like. The cation portion of the salt may include cations such as ammonium, alkylammoniums (e.g., tetraalkylammoniums, pyridiniums, and the like), alkali metals, alkaline earth metals, or the like. Cation examples include NH_4 , NBu_4 , NMe_4 , Li, Na, K, Cs, Mg, and Ca cations. Buffers may preferably contain a combination of more than one suitable salt. Typically, the concentration of buffer in the solvent is from about 0.0001 M to about 1 M, preferably from about 0.0005 M to about 0.3 M. The buffer useful in this invention may also include the addition of ammonia gas or ammonium hydroxide to the reaction system. For instance, one may use a pH = 12-14 solution of ammonium hydroxide to balance the pH of the reaction system. More preferred buffers include alkali metal phosphate, ammonium phosphate, and ammonium hydroxide buffers.

The process of the invention may be carried out in a batch, continuous, or semi-continuous manner using any appropriate type of reaction vessel or apparatus such as a fixed-bed, transport bed, fluidized bed, stirred slurry, or CSTR reactor. The catalyst is preferably in the form of a suspension or fixed-bed. Known methods for conducting catalyzed epoxidations of olefins using an oxidizing agent will generally also be suitable for use in this process. Thus, the reactants may be combined all at once or sequentially.

Epoxidation according to the invention is carried out at a temperature effective to achieve the desired olefin epoxidation, preferably at temperatures in the range of 0-150°C, more preferably, 20-120°C. Reaction or residence times of from about 1 minute to 48 hours, more preferably 1 minute to 8 hours will typically be appropriate. It is advantageous to work at a pressure of 1 to 200 atmospheres, although the reaction can also be performed at atmospheric pressure.

The following examples merely illustrate the invention. Those skilled in the art will recognize many variations that are within the spirit of the invention and scope of the claims.

5 COMPARATIVE EXAMPLE 1: PREPARATION OF TS-1 CATALYST WITHOUT
LIQUID POLYMER

TS-1 may be prepared according to any standard procedure. A typical procedure follows:

10 A dry 3-gallon stainless steel container, with a nitrogen purge, agitator, thermocouple, addition ports and valves is set in an ice bath to cool it to 0°C. The container is purged under nitrogen feed, tetraethyl orthosilicate (TEOS, 2110 g) is charged to the vessel, and the agitator is run at 1000 rpm. Tetraethyl orthotitanate (TEOT, 61 g) is then added over 30 to 60 minutes, with vigorous mixing, while maintaining the ice bath cooling. A 25 wt.% aqueous solution of
15 tetrapropyl ammonium hydroxide (TPAOH, prepared by adding 2317 g of 40 wt.% aqueous TPAOH and 1390 g of deionized water) is then added to the TEOS/TEOT mixture over 2 hours, with continued cooling. After TPAOH addition, the ice bath is removed and stirring is continued until the mixture reaches room temperature. A clear gel mother liquor is obtained.

20 A portion (200 g) of the resulting clear gel is charged into a 450-mL Parr reactor. After the reactor is closed and flushed with nitrogen, the reactor contents are heated to 180°C in 30 minutes, then held at 180°C for 6 hours with mixing at 720 rpm. After cooling the reactor to room temperature, the solid is isolated by centrifugation, washed twice with distilled water, and dried in a
25 vacuum oven at 60-70°C to constant weight (26 g). The solids are heated under nitrogen at 550°C for 4 hours, and then calcined in air at 110°C for 2 hours and at 550°C for 4 hours to produce Comparative Catalyst 1. This catalyst contains about 100% of particles having size from 0.2 to 0.9 micron.

30 EXAMPLE 2: PREPARATION OF TS-1 CATALYST USING LIQUID POLYMER

Catalyst 2A: Clear gel (200 g, from Comparative Example 1) and liquid polyisobutylene (15 g, MW 500, Polysciences, Inc.) are charged into a 450-mL Parr reactor. After the reactor is closed and flushed with nitrogen, the reactor contents are heated to 180°C in 30 minutes, then held at 180°C for 6 hours with

mixing at 620 rpm. After cooling the reactor to room temperature, the clear liquids are decanted and the solid is dried in a vacuum oven at 60-70°C to constant weight (25 g). The solid is heated under nitrogen at 550°C for 4 hours, and then calcined in air at 110°C for 2 hours and at 550°C for 4 hours to produce
5 Catalyst 2A. This catalyst contains about 75% of particles having size from 5 to 500 microns.

Catalyst 2B: Clear gel (60 g, from Comparative Example 1) and polyisobutylene (91 g, MW 500, Polysciences, Inc.) are charged into a 450-mL
10 Parr reactor. After the reactor is closed and flushed with nitrogen, the reactor contents are heated to 180°C in 30 minutes, held at 180°C for 6 hours with mixing at 620 rpm. After cooling the reactor to room temperature, the clear liquids are decanted and the solids are washed with hexane. The clear liquid is decanted and the solids are dried in a vacuum oven at 60-70°C to constant
15 weight (7 g). The solids are heated under nitrogen at 550°C for 4 hours, and then calcined in air at 110°C for 2 hours and at 550°C for 4 hours to produce Catalyst 2B. This catalyst contains about 90% of particles having size from 5 to 500 microns.

20 COMPARATIVE EXAMPLE 3: PREPARATION OF TS-1 CATALYST WITH HYDROCARBON AND SURFACTANT

Clear gel (274 g, Comparative Example 1), Igepal CO-720 (55 g, polyoxyethylene(12)nonylphenyl ether, product of Aldrich), heptane (320 g), and Polywax 1000 polyethylene (2.3 g, Baker Petrolite) are charged into a 1-L PPI
25 reactor. After the reactor is closed and flushed with nitrogen, the reactor is heated to 180°C over 2 hours ramping, and held at 180°C for 10 hours with mixing at 700 rpm. After cooling the reactor to room temperature, the solid is isolated by centrifugation, washed twice with distilled water, and dried in a vacuum oven at 60-70°C to constant weight (25 g). The solid is calcined in air at
30 110°C for 2 hours and at 550°C for 4 hours to produce Comparative Catalyst 3. This catalyst contains about 100% of particles having size from 0.3 to 1.1 micron.

EXAMPLE 4: PREPARATION OF TS-1 CATALYST WITH LIQUID POLYBUTADIENE AND SURFACTANT

Clear gel (100 g, Comparative Example 1), Igepal CO-720 (24 g, polyoxyethylene(12)nonylphenyl ether, product of Aldrich), liquid polybutadiene (110 g, 5000 MW, Aldrich), and Polywax 1000 polyethylene (1 g, Baker Petrolite) are charged into a 450-mL Parr reactor. After the reactor is closed and flushed with nitrogen, the reactor is heated to 180°C over 80 minutes ramping, and held at 180°C for 4.5 hours with mixing at 700 rpm. After cooling the reactor to room temperature, the solid is isolated by centrifugation, washed twice with distilled water, and dried in a vacuum oven at 60-70°C to constant weight (13.6 g). The solid is calcined in air at 110°C for 2 hours and at 550°C for 4 hours to produce Catalyst 4. This catalyst contains about 40% of particles having size from 5 to 100 microns.

EXAMPLE 5: EPOXIDATION OF PROPYLENE

A 100-mL Parr reactor is charged with a 70:25:5 wt.% solution of methanol/water/hydrogen peroxide (40 g) and catalyst (0.15 g). The reactor is sealed and charged with propylene (23 to 25 g). The magnetically stirred reaction mixture is heated at 50°C for 30 minutes at a reactor pressure about 280 psig, and is then cooled to 10°C. The liquid and gas phases are analyzed by gas chromatography. Propylene oxide and equivalents ("POE") are produced during the reaction. POE produced include propylene oxide ("PO") and the ring-opened products propylene glycol and glycol ethers. Results appear in Table 1.

EXAMPLE 6: PROPYLENE OXIDE RING-OPENING MEASUREMENT

A one-liter high-pressure glass reactor is charged with deionized water (30 g), methanol (119 g), acetonitrile (1.5 g) and catalyst (4.5 g). After the reactor is closed and flushed with nitrogen, the reactor is stirred and heated to 50°C. Propylene oxide (4.5 g) is added to the reactor by means of a hypodermic needle. The liquid is analyzed by gas chromatography to measure propylene oxide concentration [PO] versus reaction time. To determine the rate constant of Ring Opening, a plot of $-\ln[PO]$ versus reaction time (min) is prepared. The slope of the line is the Ring Opening rate constant. The smaller values correspond to lower Ring Opening rates. Results appear in Table 1.

The results show that catalysts produced in the presence of a hydrophobic hydrocarbon liquid polymer have a large particle size, and give high productivity and PO/POE selectivity, with a surprisingly reduced ring-opening rate constant compared to titanium zeolite produced without liquid polymer.

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TABLE 1: EPOXIDATION AND RING-OPENING RESULTS

Catalyst	H ₂ O ₂ Conversion (%)	PO produced (mmol)	POE produced (mmol)	PO/POE Selectivity (%) ¹	Ring-opening Rate Constant
1A *	85.6	47.2	50.1	94.1	0.0049
2A	65.9	43.1	46.0	93.8	0.0034
2B	73.8	42.1	43.5	96.8	0.0023
3 *	62.8	38.6	39.1	98.8	0.0013
4	52.9	30.9	31.2	99.1	0.0008

10 * Comparative Example

¹ PO/POE Selectivity = moles PO/(moles PO + moles glycols + moles glycol ethers) * 100.

I claim:

1. A process for producing a titanium or vanadium zeolite comprising reacting a titanium or vanadium compound, a silicon source, a templating agent, and a hydrophobic hydrocarbon liquid polymer at a temperature and for a time
5 sufficient to form a molecular sieve.
2. The process of claim 1 wherein the titanium compound is selected from the group consisting of titanium halides, titanium alkoxides, and mixtures thereof and the silicon source is selected from the group consisting of colloidal silica, fumed silica, silicon alkoxides, and mixtures thereof.
- 10 3. The process of claim 1 wherein the templating agent is selected from the group consisting of tetraalkylammonium hydroxides, tetraalkylammonium halides, and mixtures thereof.
4. The process of claim 1 wherein the liquid polymer is selected from the group consisting of liquid polyisobutylene and liquid polybutadiene.
- 15 5. The process of claim 4 wherein the liquid polymer is liquid polyisobutylene.
6. The process of claim 1 wherein the titanium or vanadium compound, the silicon source, the templating agent, and the liquid polymer are reacted in the presence of a surfactant.
- 20 7. The process of claim 6 wherein the surfactant is selected from the group consisting of polyoxyethylene polyoxypropylene alkyl ether, polyoxyethylene alkyl ether, polyoxyethylene alkylallyl ether, polyoxyethylene alkylaryl ether, polyoxyethylene nonylphenyl ether, polyoxyethylene octylphenyl ether, alkylene oxide adducts of acetylenic diols, and mixtures thereof.
- 25 8. A titanium or vanadium zeolite produced by the process of claim 1.
9. A process for producing an epoxide comprising reacting an olefin and hydrogen peroxide in the presence of a titanium or vanadium zeolite, wherein the titanium or vanadium zeolite is produced by reacting a titanium or vanadium compound, a silicon source, a templating agent, and a hydrophobic
30 hydrocarbon liquid polymer at a temperature and for a time sufficient to form a molecular sieve.
10. The process of claim 9 wherein the liquid polymer is selected from the group consisting of liquid polyisobutylene and liquid polybutadiene.

11. The process of claim 10 wherein the liquid polymer is liquid polyisobutylene.

12. The process of claim 9 wherein the titanium or vanadium zeolite is titanium silicalite.

5 13. The process of claim 9 wherein the olefin is a C₂-C₆ olefin.

14. The process of claim 9 wherein the reaction of olefin and hydrogen peroxide is performed in a solvent selected from the group consisting of water, C₁-C₄ alcohols, CO₂, and mixtures thereof.

10 15. The process of claim 9 wherein the hydrogen peroxide is formed by the in situ reaction of hydrogen and oxygen in the presence of a noble metal catalyst, wherein the noble metal catalyst comprises a noble metal and a support selected from the group consisting of carbon, titania, zirconia, niobium oxides, silica, alumina, silica-alumina, tantalum oxides, molybdenum oxides, tungsten oxides, titania-silica, zirconia-silica, niobia-silica, and mixtures thereof.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/004448

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J29/035 B01J29/89 C01B37/00 C07D301/12 B01J29/04

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)

B01J C01B C07D

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2007/058709 A (LYONDELL CHEMICAL TECH LP [US]) 24 May 2007 (2007-05-24) page 3, line 19 - line 29; claims 1,4-25; examples	1-15
X	EP 1 314 475 A (POLIMERI EUROPA SPA [IT]) 28 May 2003 (2003-05-28) paragraphs [0031], [0044]; claims 1,2,11,17; examples	1-8
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2009/004448

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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