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ORGANOSULFUR OXIDATION PROCESS

FIELD OF THE INVENTION

This invention relates to a process for oxidizing organosulfur impurites found in fuel streams. The process comprises reacting the organosulfur impurities with an organic hydroperoxide in the presence of a titanium-containing catalyst. The titanium-containing catalyst is obtained by impregnating a siliceous solid with a titanium halide in a hydrocarbon solvent, or a vapor stream of titanium tetrachloride, followed by calcination. The catalyst is particularly effective at oxidizing the sulfur impurities found in fuels.

BACKGROUND OF THE INVENTION

Hydrocarbon fractions produced in the petroleum industry are typically contaminated with various sulfur impurities. These hydrocarbon fractions include diesel fuel and gasoline, including natural, straight run and cracked gasolines. Other sulfur-containing hydrocarbon fractions include the normally gaseous petroleum fraction as well as naphtha, kerosene, jet fuel, fuel oil, and the like. The presence of sulfur compounds is undesirable since they result in a serious pollution problem. Combustion of hydrocarbons containing these impurities results in the release of sulfur oxides which are noxious and corrosive.

Federal legislation, specifically the Clean Air Act of 1964 as well as the amendments of 1990 and 1999 have imposed increasingly more stringent requirements to reduce the amount of sulfur released to the atmosphere. The United States Environmental Protection Agency has lowered the sulfur standard for diesel fuel to 15 parts per million by weight (ppmw), effective in mid-2006, from the present standard of 500 ppmw. For reformulated gasoline, the current standard of 300 ppmw has been lowered to 30 ppmw, effective Jan. 1, 2004.

Because of these regulatory actions, the need for more effective desulfurization methods is always present. Processes for the desulfurization of hydrocarbon fractions containing organosulfur impurities are well known in the art. The most common method of desulfurization of fuels is hydrodesulfurization, in which the fuel is reacted with hydrogen gas at elevated temperature and high pressure in the presence of a costly catalyst. U.S. Pat. No. 5,985,136, for example, describes a hydrodesulfurization process to reduce

sulfur level in naptha feedstreams. Organic sulfur is reduced by this reaction to gaseous H_2S, which is then oxidized to elemental sulfur by the Claus process. Unfortunately, unreacted H_2S from the process is harmful, even in very small amounts. Although hydrodesulfurization readily converts mercaptans, thioethers, and disulfides, other organsulfur compounds such as substituted and unsubstituted thiophene, benzothiophene, and dibenzothiophene are difficult to remove and require harsher reaction conditions.

Because of the problems associated with hydrodesulfurization, research continues on other sulfur removal processes. For instance, U.S. Pat. No. 6,402,939 describes the ultrasonic oxidation of sulfur impurities in fossil fuels using hydroperoxides, especially hydrogen peroxide. These oxidized sulfur impurities may be more readily separated from the fossil fuels than non-oxidized impurities. Another method involves the desulfurization of hydrocarbon materials where the fraction is first treated by oxidizing the sulfur-containing hydrocarbon with an oxidant in the presence of a catalyst. U.S. Pat. No. 3,816,301, for example, discloses a process for reducing the sulfur content of sulfur containing hydrocarbons by oxidizing at least of portion of the sulfur impurities with an organic hydroperoxide such as t-butyl hydroperoxide in the presence of certain catalysts. The catalyst described is preferably a molybdenum-containing catalyst.

In sum, new methods to oxidize the sulfur compound impurities in hydrocarbon fractions are required. Particularly required are processes which effectively oxidize the difficult to oxidize thiophene impurities. We have discovered an effective process for oxidizing organosulfur impurites found in fuel streams.

SUMMARY OF THE INVENTION

This invention is a process for oxidizing organosulfur impurites found in fuel streams to sulfones. The process comprises oxidizing the organosulfur impurities in the presence of an organic hydroperoxide and a titanium-containing catalyst. The titanium-containing catalyst is obtained by the method comprising: (a) impregnating an inorganic siliceous solid with a titanium source; (b) calcining the impregnated solid; and (c) optionally, heating the catalyst in the presence of water. The titanium source can be either a solution of a titanium halide in a non-oxygenated hydrocarbon solvent or a vapor stream of titanium tetrachloride.

Optionally, the catalyst preparation method comprises the additional step of treating the catalyst with a silylating agent. The catalyst is particularly effective at oxidizing the sulfur impurities found in fuels. The sulfones may then be extracted from the fuel stream to form a purified fuel stream.

DETAILED DESCRIPTION OF THE INVENTION

The oxidation process of the invention utilizes a titanium-containing heterogeneous catalyst that has unexpectedly been found to give superior oxidation performance compared to materials made using other impregnation methods. The catalyst useful in the invention is prepared by impregnating an inorganic siliceous solid with a titanium halide.

The impregnation step may be performed by impregnating an inorganic siliceous solid with a solution of titanium halide in a non-oxygenated hydrocarbon solvent. Suitable solvents for this purpose are those hydrocarbons that do not contain oxygen atoms, are liquid at ambient temperatures, and are capable of solubilizing the titanium halide. Generally speaking, it will be desirable to select hydrocarbon solvents wherein titanium halide concentrations of at least 0.5 percent by weight at 25°C can be achieved. The hydrocarbon solvent should preferably be relatively volatile so that it may be readily removed from the inorganic siliceous solid following impregnation. Solvents having normal boiling points of from 25°C to 150°C thus may advantageously be utilized. Particularly preferred classes of hydrocarbons include C_5-C_{12} aliphatic hydrocarbons (straight chain, branched, or cyclic), C_6-C_{12} aromatic hydrocarbons (including alkyl-substituted aromatic hydrocarbons), C_1-C_{10} halogenated aliphatic hydrocarbons, and C_6-C_{10} halogenated aromatic hydrocarbons. Most preferably, the solvent does not contain elements other than carbon, hydrogen, and (optionally) halogen. If halogen is present in the solvent, it is preferably chloride.

Mixtures of non-oxygenated hydrocarbons may be used, if so desired. Preferably, the solvent used for impregnation purposes is essentially free of water (i.e., anhydrous). While oxygen-containing hydrocarbons such as alcohols, ethers, esters, ketones and the like could be present in admixture with the required non-oxygenated hydrocarbon, in one desirable embodiment of the invention only non-oxygenated hydrocarbon is present as a solvent during impregnation. Examples of suitable hydrocarbon solvents include n-hexane, n-heptane, cyclopentane, methyl pentanes, methyl cyclohexane, dimethyl

hexanes, toluene, xylenes, methylene chloride, chloroform, dichloroethanes, chlorobenzene, benzyl chloride, and the like.

The impregnation process in preferred embodiments is characterized by the substantial exclusion of water until at least after impregnation is completed and preferably until after calcination. "Substantial exclusion" in the context of this invention means that water is not deliberately added or introduced or, if deliberately added or introduced, is removed prior to introduction of titanium halide. The use of reagents and starting materials having water present at the trace levels normally and customarily found in such substances when sold on a commercial scale is within the scope of the present invention. Preferably, less than 500 ppm water (more preferably, less than 100 ppm water) is present in the non-oxygenated hydrocarbon.

Suitable titanium halides include tri- and tetra-substituted titanium complexes that have from one to four halide substituents with the remainder of the substituents, if any, being alkoxide or amino groups. Suitable titanium halides include titanium tetrachloride, titanium tetrafluoride, titanium tetrabromide, titanium tetraiodide, titanium trichloride, as well as the mixed halides of Ti(III) or Ti(IV) titanium halides, diisopropoxytitanium dichloride, bis(diethylamino)titanium dichloride, and the like. Preferably, all the substituents attached to titanium are halide. Most preferably, the titanium halide is titanium tetrachloride.

While the concentration of titanium halide in the hydrocarbon solvent is not critical, the titanium halide concentration will typically be in the range of from 0.01 moles/liter to 1.0 moles/liter. The concentration of the titanium halide in the hydrocarbon solvent and the amount of solution used is desirably adjusted to provide a titanium content in the final catalyst of from 0.1 to 15 percent by weight (calculated as Ti based on the total weight of the catalyst). Multiple impregnations, with or without intervening drying and/or calcination, may be used to achieve the desired titanium content.

Suitable inorganic siliceous solids for purpose of this invention are solid materials that contain a major proportion of silica (silicon dioxide) and have a specific surface area of at least 50 m^2/g, and preferably the average specific surface area of from 300 m^2/g to 2000 m^2/g. The inorganic siliceous solids are

porous, in that they have numerous pores, voids, or interstices throughout their structures.

Synthetic inorganic oxide materials containing a major proportion of silica comprise another class of inorganic siliceous solids. Such materials are known as refractory oxides and includes silica-alumina, silica-magnesia, silica-zirconia, silica-alumina-boric and silica-alumina-magnesia. Molecular sieves, particularly large pore or mesoporous molecular sieves such as MCM-41, MCM-48 and M41S, may also be utilized as the inorganic siliceous solid.

Preferred inorganic siliceous solids are silica and mesoporous molecular sieves such as MCM-41, MCM-48 and M41S. Particularly preferred are silica and MCM-41.

It is highly desirable to dry the inorganic siliceous solid prior to impregnation. Drying may be accomplished, for example, by heating the inorganic siliceous solid for several hours at a temperature of 100°C to 700°C, preferably at least 200°C. Generally speaking, there is no need to employ temperatures in excess of 700°C in order to attain a sufficient degree of dryness. Vacuum or a flowing stream of a dry gas such as nitrogen may be applied to accelerate the drying process.

Any of the conventionally employed means of impregnating a porous solid with a soluble impregnating agent may be used. For example, the titanium halide may be dissolved in the hydrocarbon solvent and then added to or otherwise combined with the inorganic siliceous solids. The inorganic siliceous solids could also be added to the hydrocarbon solution of the titanium halide.

"Incipient wetness" impregnation techniques, whereby a minimum quantity of solvent is utilized in order to avoid formation of a slurry, are also suitable for use. The resulting mixture may be aged, optionally with agitation or other mixing, prior to further processing. Generally speaking, the impregnating solution should be placed in contact with the inorganic siliceous solids for a period of time sufficient for the solution to completely penetrate the available pore volume of the solids. The hydrocarbon solvent used for impregnation may thereafter be removed by drying at moderately elevated temperature (e.g., 50°C to 200°C) and/or reduced pressure (e.g., 1mm Hg to 100mm Hg) prior to calcination. The conditions in the solvent removal step are preferably selected so that at least 80%, more preferably at least 90%, of the hydrocarbon solvent

used for impregnation is removed prior to calcination. The drying step may be preceded by decantation, filtration or centrifugation to remove any excess impregnation solution. Washing of the impregnated siliceous solid is not necessary. Thus, one desirable embodiment of this invention is characterized by the absence of such a washing step.

The catalyst useful in the invention may also be prepared by impregnating an inorganic siliceous solid with a vapor stream of titanium tetrachloride. The vapor stream is provided by flowing a gas over liquid titanium tetrachloride. The vaporization is conducted at temperatures greater than 50°C at atmospheric pressure. Preferably, the vaporization temperature is greater than 80°C and, most preferably, greater than 130°C. Alternatively, lower temperatures are possible by decreasing reaction pressure. Preferably, the gas is an inert gas such as nitrogen, helium, argon, carbon dioxide, and the like. The vapor stream of titanium tetrachloride is then passed over the high surface area inorganic siliceous solid to complete the impregnation step. The inorganic siliceous solid is maintained at a temperature greater than 50°C during the impregnation. Preferably, the temperature of impregnation is maintained at greater than 80°C and, most preferably, greater than 130°C.

Following impregnation, the vapor phase and liquid phase impregnated siliceous solids are calcined by firing at an elevated temperature. Calcination may be performed in the presence of oxygen (from air, for example) or, more preferably, an inert gas which is substantially free of oxygen such as nitrogen, argon, neon, helium or the like or mixture thereof. In one embodiment of the invention, calcination is first performed in a substantially oxygen-free atmosphere with oxygen being introduced thereafter. Preferably, the calcination atmosphere contains less than 10,000 ppm mole oxygen. More preferably, less than 2000 ppm mole oxygen is present in the calcination atmosphere. Ideally, the oxygen concentration during calcination is less than 500 ppm. It is recognized, however, that substantially oxygen-free conditions are difficult to attain in large-scale commercial operations. Optionally, the calcination may be performed in the presence of a reducing gas, such as carbon monoxide, when the some oxygen (e.g., up to 25,000 ppm mole) is present. The optimum amount of the reducing gas will, of course, vary depending upon a number of factors including the oxygen concentration in the calcination atmosphere and the

identity of the reducing gas, but reducing gas levels of from 0.1 to 10 mole % in the calcination atmosphere are typically sufficient. In one embodiment of the invention, calcination is performed in an atmosphere comprised of oxygen, a reducing gas (preferably carbon monoxide) and, optionally, one or more inert gases (e.g., nitrogen, helium, argon, carbon dioxide).

The catalyst may be maintained in a fixed bed during calcination with a stream of gas being passed through the catalyst bed. To enhance the oxidation activity of the catalyst, it is important that the calcination be performed at a temperature of at least 500°C. More preferably, the calcination temperature is at least 700°C but no greater than 1000°C. Typically, calcination times of from about 0.1 to 24 hours will be sufficient.

The catalyst may be reacted with water after and/or during calcination. Such reaction can be effected by, for example, contacting the catalyst with steam at an elevated temperature (preferably, a temperature in excess of 100°C, more preferably, a temperature in the range of 150°C to 650°C) for from about 0.1 to 6 hours. Reaction with water is desirable in order to reduce the amount of residual halide in the catalyst derived from the titanium halide reagent and to increase the hydroxy density of the catalyst.

The catalyst may also be treated with an organic silylating agent at elevated temperature. Silylation is preferably performed after calcination and most preferably after both calcination and reaction with water. Suitable silylation methods adaptable for use in the present invention are described in U.S. Pat. Nos. 3,829,392 and 3,923,843. Suitable silylating agents include organosilanes, organohalosilanes, and organodisilazanes.

Organosilanes containing from one to three organic substituents may be utilized, including, for example, chlorotrimethylsilane, dichlorodimethyl silane, nitrotrimethyl-silane, chlorotriethylsilane, chlorodimethylphenylsilane and the like. Preferred organohalosilane silylating agents include tetra-substituted silanes having from 1 to 3 halo substituents selected from chlorine, bromine, and iodine with the remainder of the substituents being methyl, ethyl, phenyl or a combination thereof.

Organodisilazanes are represented by the formula $R_3Si\text{-}NH\text{-}SiR_3$, wherein the R groups are independently hydrocarbyl groups (preferably, C_1-C_4 alkyl) or

hydrogen. Especially preferred for use are the hexaalkyl substituted disilazanes such as, for example, hexamethyldisilazane.

Treatment with the silylating agent may be performed either in the liquid phase (i.e., where the silylating agent is applied to the catalyst as a liquid, either by itself or as a solution in a suitable solvent such as a hydrocarbon) or in the vapor phase (i.e., where the silylating agent is contacted with the catalyst in the form of a gas). Treatment temperatures are preferably in the range of from about 80°C to 450°C, with somewhat higher temperatures (e.g., 300°C to 425°C) being generally preferred wherein the silylating agent is an organohalosilane and somewhat lower temperatures (e.g., 80°C to 300°C) being preferred for the organodisilazanes. The silylation may be carried out in a batch, semi-continuous, or continuous manner.

The length of time required for the silylating agent to react with the surface of the catalyst depends in part on the temperature and agent employed. Lower temperatures generally require longer reaction times. Generally, times of from 0.1 to 48 hours are suitable.

The amount of silylating agent employed can vary widely. Suitable amounts of silylating agent can range from about 1 percent by weight (based on the weight of the entire catalyst composition) to about 75 percent by weight, with amounts of from 2 to 50 percent by weight typically being preferred. The silylating agent can be applied to the catalyst either in one treatment or a series of treatments.

The catalyst composition obtained by the aforedescribed procedure will generally have a composition comprising from about 0.1 to 15 percent (preferably, 1 to 10 percent) by weight titanium (in the form of titanium oxide, typically, and preferably, in a high positive oxidation state). Where the catalyst has been silylated, it will typically also contain 1 to 20 percent by weight carbon in the form of organic silyl groups. Relatively minor quantities of halide (e.g., up to about 5000 ppm) may also be present in the catalyst.

The catalyst compositions may optionally incorporate non-interfering and/or catalyst promoting substances, especially those which are chemically inert to the oxidation reactants and products. The catalysts may contain minor amounts of promoters, for example, alkali metals (e.g., sodium, potassium) or alkaline earth metals (e.g., barium, calcium, magnesium) as oxides or

hydroxides. Alkali metal and/or alkaline earth metal levels of from 0.01 to 5% by weight based on the total weight of the catalyst composition are typically suitable.

The catalyst compositions may be employed in any convenient physical form such as, for example, powder, flakes, granules, spheres or pellets. The inorganic siliceous solid may be in such form prior to impregnation and calcination or, alternatively, be converted after impregnation and/or calcination from one form to a different physical form by conventional techniques such as extrusion, pelletization, grinding or the like.

The organosulfur oxidation process of the invention comprises contacting a fuel stream that contains organosulfur impurites with an organic hydroperoxide in the presence of the titanium-containing catalyst. Suitable fuel streams include diesel fuel and gasoline, including natural, straight run and cracked gasolines. Other sulfur-containing hydrocarbon fractions include the normally gaseous petroleum fraction as well as naphtha, kerosene, jet fuel, fuel oil, and the like. Diesel fuel is a particularly preferred fuel stream.

Preferred organic hydroperoxides are hydrocarbon hydroperoxides having from 3 to 20 carbon atoms. Particularly preferred are secondary and tertiary hydroperoxides of from 3 to 15 carbon atoms. Exemplary organic hydroperoxides suitable for use include t-butyl hydroperoxide, t-amyl hydroperoxide, cyclohexyl hydroperoxide, ethylbenzene hydroperoxide, and cumene hydroperoxide. T-butyl hydroperoxide is especially useful.

Organic hydroperoxides are typically produced by oxidation of the corresponding alkane with coproduction of the corresponding alcohol. For example, the oxidation of isobutane produces a mixture of t-butyl hydroperoxide and t-butanol. Although it is suitable to use the organic hydroperoxide with the corresponding alcohol in the organosulfur oxidation process of the invention, it is preferable that the organic peroxide is substantially alcohol-free before use in the oxidation process. By "alcohol free", it is meant that the organic hydroperoxide:alcohol molar ratio is greater than about 25:1.

In such an oxidation process the sulfur compound:hydroperoxide molar ratio is not particularly critical, but it is preferable to employ a molar ratio of approximately 2:1 to about 1:2.

The oxidation reaction is conducted in the liquid phase at moderate temperatures and pressures. Suitable reaction temperatures vary from 0°C to 200°C, but preferably from 25°C to 150°C. The reaction is preferably conducted at or above atmospheric pressure. The precise pressure is not critical. The titanium-containing catalyst composition, of course, is heterogeneous in character and thus is present as a solid phase during the oxidation process of this invention. Typical pressures vary from 1 atmosphere to 100 atmospheres.

The oxidation reaction may be performed using any of the conventional reactor configurations known in the art for such oxidation processes. Continuous as well as batch procedures may be used. For example, the catalyst may be deployed in the form of a fixed bed or slurry.

The oxidation process of the invention converts a substantial portion of the organosulfur impurities into sulfones. Typically, greater than about 50 percent of the organosulfur impurities are converted into sulfones, preferably greater than about 80 percent, and most preferably greater than about 90 percent. When the oxidation has proceeded to the desired extent, the product mixture may be treated to remove the sulfones from the fuel stream. Typical sulfone removal processes include solid-liquid extraction using absorbents such as silica, alumina, polymeric resins, and zeolites. Alternatively, the sulfones can be removed by liquid-liquid extraction using polar solvents such as methanol, dimethyl formamide, N-methylpyrrolidone, or acetonitrile. Other extraction media, both solid and liquid, will be readily apparent to those skilled in the art of extracting polar species.

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.

EXAMPLE 1: CATALYST PREPARATION IN ACCORDANCE WITH THE INVENTION

Catalyst 1A: The silica support (Grace Davison DAVICAT P-732, particle size 0.6 -1.4 mm, surface area 300 m^2/g) is dried at 400°C in air for 4 hours. The dried silica (47 g) is charged into a 1-L round-bottom flask. A solution containing titanium (IV) diisopropoxide bis(acetylacetonate) (15.1 g, 75% solution in isopropanol) and isopropanol (89 g) is then added to the silica and mixed well. The solvent is removed by rotavaping at 90°C. The impregnated

material was calcined in air at 800°C for 2 hours. Non-silylated Catalyst 1A was measured to contain 3.2 wt.% Ti and <0.1 wt.% C.

Catalyst 1B: Silylated Catalyst 1B is made by the procedure for non-silylated Catalyst 1A, except that the silica is dried at 450°C and 51 g of the dried silica is impregnated with a solution containing titanium (IV) diisopropoxide bis(acetylacetonate) (16.3 g, 75% solution in isopropanol) and isopropanol (82 g). The catalyst is then silylated by charging the material into a 500-mL 3-neck round-bottom flask equipped with a condenser, a thermometer, and an inert gas inlet. The flask is charged with the nonsilylated catalyst (52.9 g) and hexamethyldisilazane (9.03 g) and n-heptane (99 g). The system is heated with an oil bath to reflux (98°C) under inert atmosphere for 2 hours. The system is cooled down under inert gas atmosphere and the catalyst is filtered and washed with heptane (100 mL). Obtained silylated Catalyst 1B is then dried in a flask under inert gas flow at 180-200°C for 2 hours. Measured Ti, 2.73 wt%; C, 2.0 wt%.

Catalyst 1C: Silica (Grace Davison DAVICAT P-732) is dried at 400°C in air for 4 hours. The dried silica (39.62 g) is charged into a 500-mL 3-neck round-bottom flask equipped with an inert gas inlet, a gas outlet, and a scrubber containing aqueous sodium hydroxide solution. Into the flask described above, a solution consisting of n-heptane (84.21 g, 99+%, water <50 ppm) and titanium (IV) tetrachloride (5.02 g) is added under dry inert gas atmosphere. The mixture is mixed well by swirling. The solvent is removed by heating with an oil bath at 125°C under nitrogen flow for 1.5 hours.

A portion of above material (35 g) is calcined by charging it into a tubular quartz reactor (1 inch ID, 16 inch long) equipped with a thermowell, a 500 mL 3-neck round-bottom flask, a heating mantle, an inert gas inlet, and a scrubber (containing sodium hydroxide solution). The catalyst bed is heated to 850°C under dry nitrogen (99.999%) flow (400 cc/min). After the bed is maintained at 850°C for 30 min, the power to the furnace is turned off and the catalyst bed is cooled to 400°C.

The catalyst is hydrated by the following procedure. Water (3.0 g) is added into the 3-neck round-bottom flask and the flask is heated with a heating mantle to reflux while maintaining the nitrogen flow at 400 cc/min. The water is distilled through the catalyst bed over a period of 30 minutes. A heat gun is

used to heat the round-bottom flask to ensure that any residual water is driven out of the flask through the bed. The bed is then maintained at 400°C for an additional 2 hours before cooling. Catalyst 1C contains 3.7 wt.% Ti.

Catalyst 1D: Catalyst 1C is further silylated as follows.

A 500 mL 3-neck round-bottom flask is equipped with a condenser, a thermometer, and an inert gas inlet. The flask is charged with heptane (39 g, water <50 ppm), hexamethyldisilazane (3.10 g) and Catalyst 1C (11.8 g). The system is heated with oil bath to reflux (98°C) for 2 hours under inert atmosphere before cooling. The catalyst is filtered and washed with heptane (100 mL). The material is then dried in a flask under inert gas flow at 180-200°C for 2 hours. Catalyst 1D contains 3.5 wt.% Ti and 1.97 wt.% C.

Catalyst 1E: Silica (Grace Davison DAVICAT P-732) is dried in at 450°C in air for 2 hours. The dried silica (36 g) is charged into a tubular quartz reactor (1 inch ID, 16 inch long) equipped with a thermowell, a 500-mL 3-neck round-bottom flask, a heating mantle, an inert gas inlet, and a scrubber (containing sodium hydroxide solution). The catalyst bed is heated to 300°C under dry nitrogen (99.999%) flow (400 cc/min). Titanium tetrachloride (7.4 g) is transferred to the 3-neck round-bottom flask and the flask is heated with a heating mantle to reflux while maintaining the nitrogen flow at 400 cc/min. The titanium tetrachloride is distilled through the catalyst bed in a period of 1 hour. A heat gun is used to heat the round-bottom flask to ensure that any residual titanium tetrachloride is driven out of the flask through the bed. The bed is then heated at 850°C for 0.5 hour before cooling to 400°C.

Water (3.0 g) is added into the 3-neck round-bottom flask and the flask is heated with a heating mantle to reflux while maintaining the nitrogen flow at 400 cc/min. The water is distilled through the catalyst bed over a period of 30 minutes. A heat gun is used to heat the round-bottom flask to ensure that any residual water is driven out of the flask through the bed. The heat to the heating mantle was turned off. The tube reactor was cooled to room temperature.

The catalyst is then silylated according to the procedure described for Catalyst 1B, except that 15 g of catalyst, 43 g of heptane, and 3.0 g of hexamethyldisilazane is used. Catalyst 1E contains 2.6 wt.% Ti and 2.0 wt.% C.

Catalyst 1F: MCM-41 silica support can be made according to any known literature procedure. See, for example, U.S. Pat. No. 3,556,725, DiRenzo, et. al., Microporous Materials (1997), Vol. 10, 283, or Edler, et. al., J. Chem. Soc., Chem. Comm. (1995), 155. The obtained MCM-41 gel is dried at 180°C and then calcined at 550°C for 14 hours before use. BET surface area of the material is 1488 m^2/g. MCM-41 (4.36 g) is charged into a 500-mL 3-neck round-bottom flask equipped with an inert gas inlet, a gas outlet, and a scrubber containing aqueous sodium hydroxide solution. Into the flask described above, a solution consisting of n-heptane (60 g, 99+%, water <50 ppm) and titanium (IV) tetrachloride (0.95 g, 0.55 ml) is added under dry inert gas atmosphere. The mixture is mixed well by swirling. The solvent is removed by rotavaping under vacuum at 80°C for 1 h.

The above obtained material is then calcined and hydrated according to the procedure described for Catalyst 1C. The catalyst is then silylated according to the procedure described for Catalyst 1B, except that 3.72 g of catalyst, 35 g of heptane, and 0.96 g of hexamethyldisilazane is used. Catalyst 1F contains 5.5 wt.% Ti and 5.1 wt.% C.

EXAMPLE 2. OXIDATION OF THIOPHENES WITH TBHP OXIDATE

Catalysts 1A-F are tested in the oxidation of various organosulfur compounds. The test results are shown in Table 1. A feed is prepared by mixing either toluene or ethyl benzene with dibenzothiophene (DBT) and Lyondell TBHP oxidate (containing approximately 43 wt% TBHP and 56% tertiary butyl alcohol). The feed contains 0.175 wt.% (DBT), 0.32 wt.% t-butyl alcohol (TBA), and 0.24 wt.% t-butyl hydroperoxide (TBHP). The molar ratio of DBT to TBHP is 2.8.

Examples 2A-F: The toluene-based feed (28 g) is heated and stirred in a round-bottom flask to 50°C under nitrogen atmosphere. The Ti/silica catalyst (0.2 g, in powder form) is then added and the reaction proceeds at 50°C under nitrogen atmosphere for 0.5 hour. The reaction mixture is analyzed by GC and HPLC. Oxidation products of thiophene are found to be the corresponding sulfoxide and sulfone as determined by GC and GC-MS.

Example 2G is run under the same procedure as in Examples 2A-F except that 0.04 g of the particle form of Catalyst 1D is used, and the reaction temperature is 80°C.

Example 2H is run under the same procedure as in Example 2G except that 4,6-dimethyl dibenzothiophene (DMDBT) is used instead of DBT. The molar ratio of DMDBT to TBHP was 2.4.

Example 2I-J are run under the same procedure as in Examples 2A-F except that the ethyl benzene based solution is used, 0.02 g of the particle form of Catalyst 1D is used, the reaction temperature is 80°C, and the reaction time is one hour. For Comparative Example 2J, no catalyst is used.

TABLE 1. Organosulfur Oxidation with Ti/silica Catalysts

Run #	Catalyst	Catalyst Amount (g)	Solvent	Substrate	Temperature (°C)	Conversion (%)
2A *	1A	0.2	Toluene	DBT	50	31
2B *	1B	0.2	Toluene	DBT	50	39
2C	1C	0.2	Toluene	DBT	50	90
2D	1D	0.2	Toluene	DBT	50	91
2E	1E	0.2	Toluene	DBT	50	91
2F	1F	0.2	Toluene	DBT	50	97
2G	1D	0.04	Toluene	DBT	80	93
2H	1D	0.04	Toluene	DMDBT	80	56
2I	1D	0.02	EB	DBT	80	80
2J *	-	-	EB	DBT	80	10

* Comparative Example

We claim:

1. A process comprising contacting a fuel stream containing organosulfur impurities with an organic hydroperoxide in the presence of a catalyst obtained by a method comprising the steps of:

(a) impregnating an inorganic siliceous solid with a titanium source selected from the group consisting of:

(1) a solution of a titanium halide in a non-oxygenated hydrocarbon solvent; and

(2) a vapor stream of titanium tetrachloride;

(b) calcining the impregnated siliceous solid to form the catalyst; and

(c) optionally, heating the catalyst in the presence of water;

wherein a substantial portion of the organosulfur impurities are converted into sulfones.

2. The process of claim **1** wherein the titanium halide is titanium tetrachloride.

3. The process of claim **1** wherein impregnation step (a)(1) is accomplished by combining a solution of the titanium halide in the non-oxygenated hydrocarbon solvent with the inorganic siliceous solid and thereafter removing the hydrocarbon solvent.

4. The process of claim **1** wherein the inorganic siliceous solid is selected from the group consisting of silica and MCM-41.

5. The process of claim **1** wherein the non-oxygenated hydrocarbon solvent is selected from the group consisting of C_5-C_{12} aliphatic hydrocarbons, C_6-C_{12} aromatic hydrocarbons, C_1-C_{10} halogenated aliphatic hydrocarbons, C_6-C_{10} halogenated aromatic hydrocarbons, and mixtures thereof.

6. The process of claim **1** wherein water is substantially excluded until after step (b) is completed.

7. The process of claim **1** wherein the method of obtaining the catalyst comprises an additional step after step (c) of treating the catalyst with a silylating agent.

8. The process of claim **1** wherein calcination step (b) is performed at a temperature of at least 500°C.

9. The process of claim **1** wherein step (b) is performed in a substantially oxygen-free atmosphere.

10. The process of claim **1** wherein the organic hydroperoxide is t-butyl hydroperoxide.

11. The process of claim **1** wherein the organic hydroperoxide is substantially free of alcohol.

12. A process comprising contacting a diesel fuel stream containing organosulfur impurities with t-butyl hydroperoxide in the presence of a catalyst obtained by a method comprising the steps of:

(a) impregnating an inorganic siliceous solid with a titanium source selected from the group consisting of:

(1) a solution of a titanium chloride in a non-oxygenated hydrocarbon solvent; and

(2) a vapor stream of titanium tetrachloride;

(b) calcining the impregnated siliceous solid to form the catalyst; and

(c) optionally, heating the catalyst in the presence of water;

wherein a substantial portion of the organosulfur impurities are converted into sulfones.

13. The process of claim **12** wherein impregnation step (a)(1) is accomplished by combining a solution of the titanium halide in the non-oxygenated hydrocarbon solvent with the inorganic siliceous solid and thereafter removing the hydrocarbon solvent.

14. The process of claim **12** wherein the inorganic siliceous solid is selected from the group consisting of silica and MCM-41.

15. The process of claim **12** wherein the non-oxygenated hydrocarbon solvent is selected from the group consisting of C_5-C_{12} aliphatic hydrocarbons, C_6-C_{12} aromatic hydrocarbons, C_1-C_{10} halogenated aliphatic hydrocarbons, C_6-C_{10} halogenated aromatic hydrocarbons, and mixtures thereof.

16. The process of claim **12** wherein water is substantially excluded until after step (b) is completed.

17. The process of claim **12** wherein the method of obtaining the catalyst comprises an additional step after step (c) of treating the catalyst with a silylating agent.

18. The process of claim **12** wherein calcination step (b) is performed at a temperature of at least 500°C.

19. The process of claim **12** wherein step (b) is performed in a substantially oxygen-free atmosphere.

20. The process of claim **12** wherein the t-butyl hydroperoxide is substantially free of t-butyl alcohol.

ABSTRACT OF THE DISCLOSURE

This invention is a method of oxidizing organosulfur impurites found in fuel streams. The method comprises reacting the organosulfur impurities with an organic hydroperoxide in the presence of a titanium-containing catalyst. The titanium-containing catalyst is obtained by impregnating a siliceous solid with a titanium halide in a hydrocarbon solvent, or a vapor stream of titanium tetrachloride, followed by calcination. The resulting sulfones are more readily removed from the fuel stream than the non-oxidized organosulfur impurities.